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The Polymerization of Gaseous Butadiene*

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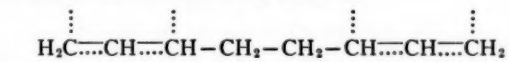
Dimerization of butadiene has been studied in the temperature range from 446 to 660°K. The rate constant is expressed approximately by the equation:

$$k_2 = 9.20 \cdot 10^9 \exp(-23{,}690/RT) \text{ cc mole}^{-1} \text{ sec.}^{-1}.$$

Deviations from this relation suggest an increase of activation energy with temperature. 3-vinyl cyclohexene formed in the dimerization reaction undergoes further addition with butadiene to give Δ3,3′-octahydro diphenyl. The rate constant of this reaction is given by the equation:

$$k_3 = 1.3 \cdot 10^{14} \exp(-38{,}000/RT) \text{ cc mole}^{-1} \text{ sec.}^{-1},$$

but the data on which it is based are not very accurate. Statistical calculation of the entropy of an activated complex which has the resonating structure



gives agreement with experimental data to within a factor of ten whereas the assumption that the reaction goes in a single step to the cyclic product gives a rate differing by more than a thousand-fold from the observed one. The role of resonating free radicals in other reactions of the dienes is discussed briefly.

A GRADUAL accumulation of experimental data on the kinetics of the 1,4–1,2 additions of dienes[1] has led to the realization that these processes are the best examples of association reactions of large molecules. They are all of the second order—in the gas phase and in solution—and are characterized by frequency factors considerably smaller than the collision numbers. In general the gas phase reactions are fairly

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[1] For a summary of the literature see Harkness, Kistiakowsky and Mears, J. Chem. Phys. **5**, 682 (1937); also G. König, *Kinetic der Polymerization der Cyclopentadienes, etc.* Inaugural-Dissertation, Friedrich-Wilhelms-Universtät (1938); Benford, Khambata and Wassermann, Nature **139**, 669 (1937); Krause, Charskaya and Korchmarek, Sintet. Kauchuk **7**, 3 (1936); Lebedev, Khokhlovkin, Kuibina and Begetova, Sintet. Kauchuk **1**, 2 (1936); J. Phys. Chem. (U. S. S. R.) **7**, 130 (1936); and Moor, Strigaleva and Shilyaeva, J. Gen. Chem. (U. S. S. R.) **5**, 818 (1935); Trans. Exptl. Research Lab. "Khemgas," Materials on Cracking and Chem. Treatment of Cracking Products (U. S. S. R.) **3**, 33 (1936).

clean, but the second-order rate constants do show marked drifts in later stages of a run.

One of the cleanest of these reactions is the dimerization of butadiene, studied by Vaughan,[2] in which only after some 50-percent conversion are the deviations from second-order appreciable. Vaughan interpreted the deviations as caused by a secondary reaction of the dimer with unreacted monomer. A different suggestion has been put forward by one of the present authors,[1] namely that an intermediate free radical undergoes an addition reaction with monomer molecules as an alternate to its isomerization into the stable cyclic dimer. The formation of the intermediate open chain radical in the course of dimerization of butadiene was inferred from qualitative considerations of the statistics of the reaction which require an accurate knowledge of the frequency factor. Vaughan's work on butadiene, as well as later experiments on other similar reactions have all been limited to rather narrow temperature ranges, which, together with the uncertainties arising from the imperfect second-order character of the reactions, make an accurate determination of activation energies, and hence of frequency factors, impossible.

The present work concerns itself with a study of the rate of butadiene dimerization over a wide temperature range and with a study of the secondary reactions accompanying dimerization.

Experimental Details

The rate of dimerization of butadiene was studied in a static system by following pressure changes. At the lower end of the temperature range covered in this work the rate constant is so small that pressures far in excess of atmospheric had to be employed to secure measurable rates. The reaction system consisted therefore of a thick-walled Pyrex bulb, to which was joined by a short capillary a rather stiff Bodenstein quartz spiral, sealed within a thick-walled Pyrex tube. The reaction bulb was within the usual electric furnace of good construction. The spiral tube was wrapped with a heating element and maintained at a constant temperature of some 175°. To the closed end of the spiral was sealed a small quartz plate acting as a mirror. A straight filament lamp and a telescope with cross hair provided means for observing the rotations of the mirror; during the runs the pressure in the tube surrounding the spiral was adjusted with the aid of a pump and oxygen cylinder, until the position of the mirror coincided with that obtaining when the pressures on both sides of the spiral were equal, and then read on a long mercury manometer. This system was sensitive enough to detect pressure changes of less than 0.5 mm and the zero point did not drift more than the equivalent of one or two mm pressure per hour.

Upon evacuation of the reaction flask a suitable quantity of butadiene was admitted through a Bodenstein glass valve (provided with a silver chloride seat) and condensed in a miniature trap permanently connected to the reaction system. After closing the valve, the trap was suddenly heated (by immersion in hot water), whereupon butadiene volatilized. This usually took from two to four minutes for completion. During the progress of the reaction the trap was kept in a small electric furnace at 175°; the glass valve and the connecting capillary tubing were also electrically heated to the same temperature. A similar procedure was used to introduce vinyl cyclohexene into the reaction system in other experiments.

Copper shields in the furnace produced temperatures uniform within 0.3°. The temperatures were measured with a chromel-copel thermocouple, calibrated before and after the experiments described below against a standard platinum resistance thermometer; all absolute temperatures should be accurate to better than 0.5°, but a greater accuracy can be claimed for the determination of relative temperatures over short intervals.

The study of the secondary reactions required that analyses of the products be made. For this purpose reaction flasks were used whose sizes varied so that at all pressures investigated about 2 to 2.5 g of butadiene could be reacted at once. The pressure measuring device was as described above. After the reaction was followed a sufficient length of time the glass valve was opened and the gases condensed by liquid air in a Y-shaped trap separated from a pump by a metal valve. In runs made at the higher temperature the metal valve leading to the pump had to be cracked

[2] W. E Vaughan, J. Am. Chem. Soc. **54**, 3863 (1932).

open to eliminate noncondensible gases which, though present in very small quantities, prevented complete condensation of the other products.

After the glass valve was closed the condensed substance was allowed to warm up until it collected in a capsule sealed to the bottom of the Y trap; this was chilled again and finally the condensed products were sealed off in it.

The sample was placed in a trap provided with a ground joint and weighed. After the trap was joined to the distilling system and evacuated, the capsule was broken magnetically. The sample was thereupon separated by fractional distillation at low pressures. The receivers, cooled in liquid air, communicated with the distilling trap by way of a three-cm length of 1.5-mm i.d. capillary tubing. This enabled control of the rate of distillation.

In the separation of monomer from dimer the temperature of the mixture was raised from $-80°$ to $-30°$ at a rate controlled so as to keep the distillation pressure below a certain minimum. After the distilling tube was maintained at that temperature for a standard time, the receiver was shut or sealed off from it and liquid air was applied to a new receiver.

Thence, in separation of dimer from higher polymers the temperature of the mixture was raised in a similar manner to $+27°$. After maintenance of the distilling tube at that temperature for a standard time, the receiver containing the dimer was sealed off, and its weight determined. Air was admitted to the distilling tube, it was removed from the line and weighed. The remaining polymeric material could be removed with benzene and its weight found after subsequent weighing of the clean distilling tube. Part of the polymer never reached the Y-shaped trap in the first condensation, settling out instead in the connecting tubing. Its weight was obtained from the difference in weights of the butadiene introduced and the total material collected in the Y trap.

Experiments with artificially prepared mixtures of butadiene and its dimer in quantities found in the actual measurements showed that this method resulted in removal of 99 percent of butadiene while the loss of dimer did not exceed 0.5 percent of the quantity originally present.

That the method was successful in separation of dimer from polymer was indicated by the facts that the dimer fraction had the refractive index of 3-vinyl cyclohexene and that the weight of the polymer fraction could not be reduced by pumping.

Several measurements of the rate of dimerization of butadiene at 446°K and 6.5 atmos. were made. Weighed quantities of butadiene were distilled into thick-walled Pyrex tubes provided with magnetic "break-off" seals and there sealed off. The tubes were placed in an oil bath with automatic temperature regulation and kept there for times varying from twelve to one hundred and twenty hours. Thereupon the reaction tubes were sealed to the fractionation apparatus described above and the "break-offs" broken. All material which was volatile at room temperature was transferred to a capsule and weighed. The products were then analyzed for monomer and dimer in the manner described. Within the limit of experimental error (i.e., less than 0.1 percent), no polymer with the properties of the material found at higher temperatures was found; however, minute traces of solid polymers were apparent as white solids on the reaction tube walls.

Several samples of butadiene were used for this work; some were part of the material prepared for the measurements of the heats of hydrogenation;[3] these were freed from polymerization products by distillation in vacuum but not further purified. Other samples were prepared from 1,2,3,4-tetrabromobutane and subjected to various purification operations, including removal of alcohol, drying and vacuum distillation. Their freezing curves, compared with those obtained with the highest purity butadiene,[4] suggested that the material was about 99 percent pure. All samples gave identical rates of reaction.

The Results

The molecular weight of the polymer recovered from fractional distillation was determined by the method of freezing-point lowering in benzene solution. Three experiments for which no great claims as to accuracy can be made gave 3.5, 5.0 and 3.6 times the molecular weight of butadiene.

[3] Kistiakowsky, Ruhoff, Smith and Vaughan, J. Am. Chem. Soc. **58**, 146 (1936).
[4] Reference 3, p. 147.

TABLE I. *Results of the analysis of the reaction products.*

T, °K	Initial Pressure mm	Percent Reaction	Polymer / Dimer	k_3
644	336	50	0.090	13
644	338	50	.093	14
644	333	85	.292	12
645	348	86	.308	13
572	326	50	.036	0.35
572	344	50	.031	0.31
573	2886	51	.024	0.33
572	2811	48	.021	0.30
572	336	85	.085	0.29
572	327	85	.095	0.34
572	2869	86	.057	0.30
571	2866	85	.059	0.31

The determinations of the composition of the reaction mixture, described above, together with the knowledge of the initial and final pressure provide an independent method for the determination of the molecular weight of the polymer. This gave 3.0 and 3.1 units of butadiene in the two experiments in which enough polymer was formed to make such calculations feasible.

It is thus evident that trimer is formed in the secondary reaction of the dimer predominantly if not exclusively. Alder and Richert[5] have studied the structure of a trimer of butadiene formed thermally in the liquid phase and have shown it to be $\Delta 3'3$-octahydro diphenyl. There can be hardly any doubt that the material recovered by us has the same structure.

The first experiments on the composition of the reaction products revealed that the ratio of trimer to dimer increases with the progress of the reaction but decreases as the initial pressure is increased for the same fraction of butadiene reacted. Kinetically this at once eliminates the intermediary free radical with its two alternate reactions as the source of trimer but confirms instead Vaughan's original suggestion.

To test this further 3-vinyl cyclohexene (prepared in other runs and purified by repeated distillations) was introduced at 200 mm into the reaction flask and was found to remain at constant pressure at the temperature of the experiment (644°K). However, upon addition of 20 mm butadiene, the pressure was found to fall off at the rate of 0.108 mm per minute. At this pressure butadiene alone polymerizes at the rate of only 0.024 mm per minute; hence an additional reaction with the dimer was taking place. The second-order rate constant was found to be roughly 13.5 cc mole^{-1} sec.$^{-1}$.

Table I shows the results of experiments on the composition of the reaction products. The weight ratios of column 4 were found after the reaction had proceeded to the approximate extent indicated by column 3.

The rate constants of the trimerization, tabulated in column 5, were found with the aid of the equation:

$$\ln\frac{B}{B_0}=\tfrac{1}{2}\ln\frac{a}{r^2+br+a}+\frac{d}{c}\ln\frac{(2r+b+c)(b-c)}{(2r+b-c)(b+c)}. \quad (1)$$

Elimination of time from the differential equations

$$\dot{B}=-k_2B^2-k_3BD, \quad (2)$$

$$\dot{D}=\frac{k_2}{2}B^2-k_3BD, \quad (3)$$

and integration of the result yields the above. Here B = pressure of butadiene at any time, D = pressure of dimer at any time, B_0 = initial pressure (of butadiene), $a=k_2/2k_3$, the ratio of dimerization to trimerization rate constants,

$$b=k_2/k_3-1,$$
$$c=[(k_2/k_3)^2-4k_2/k_3+1]^{\frac{1}{2}},$$
$$d=(k_2/k_3+1)/2,$$

and $$r=D/B.$$

The rate constants for the dimerization reaction, k_2, were taken from Table II, the pressure ratios were found from the weights of butadiene and of dimer recovered, whereupon k_3 was found by trial and error.

As Table I shows, the k_3 constants are independent of the extent of reaction and of the initial pressure in a wholly satisfactory manner. The agreement of the trimerization rate constant at 644° in Table I with that calculated above from a direct measurement of the dimer-monomer reaction is excellent proof of the correctness of the mechanism assumed for Eqs. (2) and (3). Thus the previously existing doubts about the true order of butadiene dimerization are now eliminated and the reaction is established as of strictly second order.

The structure of the trimer of butadiene indi-

[5] K. Alder and H. F. Richert, Ber. **71**, 373 (1938).

cates that its formation is another example of the 1,2–1,4 condensation reactions. From the data of Table I the activation energy is readily obtainable, and the rate constant is found to be best represented by the equation:

$$k_3 = 1.3 \cdot 10^{14} \exp(-38{,}000/RT) \text{ cc mole}^{-1} \text{ sec.}^{-1}.$$

This result is most surprising since all other condensation reactions have frequency factors of the order of 10^{10} and less; in fact, 10^{14} is as large as the collision number in the units chosen and kinetically is rather difficult to understand. It is true, of course, that the data from which these rate constants have been obtained are not very accurate, but in order to have a frequency factor of the order of 10^{10} and yet have rate constants of the order of the magnitude observed, one must decrease the activation energy until it becomes nearly equal to that of butadiene dimerization. This, however, is wholly out of the question since an increase in the relative yield of the trimer with rising temperature of the reaction is unmistakable, both from the analytical results and from the magnitude of deviations of the uncorrected dimerization rate from the second order; hence it could not be due to some unknown error of analysis.

Unfortunately the problem of the trimerization rate must be left in its present unsatisfactory state because of difficulties hindering its more accurate measurement. The explanation of the large frequency factor must also be left to the future, but we wonder whether some reaction mechanism connected with a transitory formation of free radicals may not be responsible for it.

In Table II are collected the results of experiments on the rate of dimerization of butadiene: the second-order rate constants were determined from graphs of the inverse pressure against time. As initial time the instant at which one-half of the entire butadiene was vaporized into the flask was taken. The plots gave within experimental error straight lines to about 50 percent reaction and therefore the rate constants were not extrapolated to initial time. A correction for the volume outside of the reaction flask was applied[6] but no correction was made for the trimerization reaction.

[6] A. O. Allen, J. Am. Chem. Soc. **56**, 2053 (1934).

The rate constants for the runs at 446°K were calculated from the weights of the monomer and dimer found.

The rates here reported are some 22 percent higher than those given by Vaughan for his 80-cc flask. It is to be noted, however, that his runs in a 320-cc flask gave rates 12 percent higher than the others. This leads to the conclusion that a considerable dead space correction should have been applied to his data. From the relative rates in the two flasks the correction is readily obtained and so it is found that Vaughan's corrected rates are only six percent lower than those here given. This corresponds to only 1–2° difference in the temperature scales and since Vaughan used a not specially calibrated chromel-alumel thermocouple, both researches are in satisfactory agreement. The two measurements of Lacher[7] gave rates about 60 percent lower than those found in the present work.

A logarithmic plot of the rate constants against inverse temperature does not quite give

TABLE II. *Rate of dimerization of butadiene.*

T, °K	B_0, mm	k†	Percent Deviation
446.0	5000	0.0164	−31
503.2	3151	0.531	+ 5
503.5	3158	0.517	+ 5
513.1	3067	0.751	− 2
513.3	3142	0.748	− 3
523.1	2992	1.19_1	0
527.1	3052	1.40_8	0
527.5	3038*	1.38_3	− 3
527.4	2307	1.38_8	− 3
527.4	1550	1.43_1	0
530.1	2800	1.51_4	− 6
530.9	3147	1.70_6	+ 3
538.3	2543	2.30_0	+ 2
540.3	2616	2.43_4	0
554.4	1205	3.97_6	− 7
555.2	1387	4.18_7	− 6
577.9	1186	9.81	− 6
577.9	1196	9.85	− 6
605.6	733	24.8	− 6
605.9	733	25.4	− 5
621.8	724	40.7_9	− 7
621.9	553	44.5_5	+ 1
640.1	592	82.9	+ 8
640.2	464	85.3	+11
642.5	708	84.4	+ 2
656.9	588	139	+12
659.4	443	$151._2$	+15
659.4	531	149	+13

* With 17 mm air. † k's in cc mole^{-1} sec.$^{-1}$ units.

[7] G. B. Kistiakowsky and J. R. Lacher, J. Am. Chem. Soc. **58**, 123 (1936).

a straight line, as seen in Table II, column 4 which contains percentage deviations of the observed rate constants from those interpolated by the equation:

$$\ln k_2 = -23{,}690/RT + 22.94. \qquad (4)$$

The deviations are in the direction suggesting that the activation energy of the reaction increases with increasing temperature, a conclusion not in disagreement with results of other work. Thus Lebedev[1] found an activation energy of 24,900 cal. in the temperature range 380–470°K, while Vaughan obtained 26,000 between 600 and 670°K and Moor found 28,000 cal. for the range 670–970°K. It is, however, possible that the most marked deviations from the straight line, which occur at the highest temperatures, are due to another cause. The rate constants of Table II were calculated neglecting trimerization reaction. This becomes prominent at the highest temperatures and thus leads to calculated dimerization rate constants which are too high. Attempts to fit experimental time-pressure curves allowing for both reactions indicate that the dimerization constants should be reduced here as much as five to ten percent.

The activation energy presented here is 2300 cal. lower than that given by Vaughan. This difference is due to the greater weight given by us to our low temperature measurements and, if anything, the true value is slightly higher. For the same temperature intervals both researches give identical activation energies.

The rate constant found at 446° K also deviates considerably from that calculated, but it should not be given too much weight because of a different and less accurate technique.

Interpretation of the Results

In the previous paper[1] it was suggested that the structure of the activated complex is that of an open chain, doubly unsaturated free radical stabilized by resonance. The present experiments determine the magnitude of the frequency factor with such accuracy that more elaborate statistical calculations than those made heretofore seem to be justified. However, before discussing them, we wish to return to the problem of the energetics of the radical formation. As explained in the previous paper, the condition for the radical formation is that:

$$2(B-A)+A+2R_B-R_D-24<0, \qquad (5)$$

where B is the energy needed to open a double bond to a single one and A is the energy of a single bond in the middle of a long hydrocarbon chain; thermochemical data give for $B-A$ -24.5 kcal.;* R_B is the resonance energy in butadiene; R_D is that in the free radical and 24 kcal. is the activation energy of the reaction. Recently Coulson[8] calculated the resonance by energy in a radical:

$$H_2\dot{C}-CH=CH_2$$

the method of molecular orbitals and found it equal to 15 kcal. For butadiene he obtained by the same procedure 5 kcal., a value which is probably very nearly correct[9] and is in any case not too high. Hence it is justifiable to use also his other value, doubling it because identical resonance occurs on both ends of the free radicals here involved. Substituting the figures, one finds from Eq. (5) that the energy of the single carbon-carbon bond must be less than 93 kcal. In ethane, therefore,[9] the energy must be less than 95 kcal. We believe that the carbon-carbon bond energy of ethane is at most some 80 kcal. notwithstanding Taylor's arguments in favor of nearly 100 kcal.[10] Hence, after the formation of activated complex, the free radical is stabilized by energy loss in collisions and needs then some 15 kcal. activation energy to decompose again. This gives it a reasonable lifetime to isomerize into 3-vinyl cyclohexene or to initiate the long chain polymer formation which takes place at low temperature and high concentrations. The latter, however, is sufficiently slow so that a quantitative isomerization into the cyclic product occurs under our experimental conditions.

For the purposes of a quantitative calculation of the frequency factor we shall write the statistical rate expression[11] in the form:

* The change from 22.5 given in the previous paper is due to the use of Coulson's value for the resonance energy in butadiene.

[8] C. A. Coulson, Proc. Roy. Soc. **A164**, 383 (1938).

[9] Cf. a forthcoming paper by Conn, Kistiakowsky and Smith in J. Am. Chem. Soc.

[10] Trenner, Morikawa and Taylor, J. Chem. Phys. 5, 203 (1937).

[11] H. Eyring, J. Chem. Phys. **3**, 107 (1935).

$$k=\exp(\Delta S^*/R)\cdot e^2\cdot\frac{kT}{h}\cdot\exp(-\Delta E/RT), \quad (6)$$

where ΔE is the experimental activation energy at a temperature T. It is assumed that the transmission coefficient is unity, the least favorable assumption in the present case. By comparison with Eq. (4) we see that at the mean temperature of 600° K:

$$\exp(\Delta S^*/R)\cdot e^2\cdot\frac{kT}{h}=10^{9.96}. \quad (7)$$

(I) Entropy of butadiene

Kassel[12] has calculated the translational and rotational entropy of butadiene, assuming free rotation around the central bond. The hindrance to free rotation in propylene is only 800 cal.[13] and according to the tables of Pitzer[14] this causes only some 0.05 E.U. decrease in entropy at 600°K, if the rotation in butadiene is hindered to the same extent. It is possible that the real hindrance is greater because of resonance between the double bonds, but an increase in the hindering potential is favorable to the calculation and therefore will not be introduced.

Pitzer[15] has proposed rules for approximately calculating vibrational frequencies in hydrocarbon molecules, which give satisfactory results in the several instances cited by him. We shall adopt these rules, Table III giving the results for butadiene. Combining the totals of Table III with Kassel's value for rotation and translation, the following results (the entropy is calculated for one mole per cc concentration):

$S_{600°}=67.4$ E.U.; $C_{v600°}=29.5$ cal./mole degree.

(II) Entropy of the activated complex

Considerable evidence has been accumulated to show that activated complexes have thermodynamic properties not very different from those of the stable associated molecules.[16] We shall assume for the following therefore that the activated complex is identical (except for one degree of freedom) with the resulting free radical. The translational entropy of the radical presents, of course, no difficulties, but a calculation of the rotational entropy by the procedure of Kassel is here rather involved. Therefore the over-all rotational entropy was computed as if the molecule were rigid and the internal rotation contributions were calculated as for symmetric tops.[17] The moments of inertia depend on the geometrical configuration selected from the many allowed by internal rotations. However, the variations in the individual degrees of freedom nearly compensate each other in the calculation of the total rotational entropy and the result is practically independent of the specific configuration assumed. To get a better idea of the errors ensuing from this procedure, the rotational entropy of butadiene was similarly computed and found to be lower by *ca.* 1 E.U. than that given by Kassel.

The resonance in the ends of the molecule should make the two structures:

$$H_2\overset{/}{C}-CH=CH- \quad \text{and} \quad H_2C=CH-\overset{/}{C}H-$$

wholly equivalent and the most reasonable assumption is to treat both bonds involved as having properties halfway between those of a double and those of a single bond. In calculating the thermodynamic functions of the activated complex it was assumed therefore that the distances between the three carbon atoms on each end of the molecule:

$$\overset{1}{H_2}C\cdots\overset{2}{C}H\cdots\overset{3}{C}H-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H\cdots\overset{7}{C}H\cdots\overset{8}{C}H_2$$

are 1.40A. Other carbon-carbon distances were taken as 1.53A; hydrogen atoms were treated as

TABLE III. *Vibrational entropy and heat capacity of butadiene.*

VIBRATION CLASS	NUMBER OF VIBRATIONS	FREQUENCY, CM^{-1}	S, E.U.	C, CAL./MOLE DEGREE
H−C stretching	6	3000	0.06	0.492
H−C−H bending	2	1440	0.58	1.61
H−C−C bending	8	950	5.90	10.52
C−C stretching	1	1000	0.67	1.26
C=C stretching	2	1600	0.42	1.33
C=C−C bending	2	320	5.12	3.78
C=C torsion	2	570	3.04	3.41
	23		15.79	22.40

[12] L. S. Kassel, J. Chem. Phys. **4**, 435 (1936).
[13] Kistiakowsky, Lacher and Ransom, J. Chem. Phys. **6**, 900 (1938).
[14] K. S. Pitzer, J. Chem. Phys. **5**, 469 (1937).
[15] K. S. Pitzer, J. Chem. Phys. **5**, 473 (1937).
[16] O. K. Rice and H. Gershinowitz, J. Chem. Phys. **3**, 479 (1935).
[17] K. S. Pitzer, J. Chem. Phys. **5**, 469 (1937), Eq. (2).

TABLE IV. *Vibrational entropy and heat capacity of the free radical.*

VIBRATION CLASS	NUMBER OF VIBRATIONS	FREQUENCY, cm^{-1}	S, E.U.	C, CAL./MOLE DEGREE
H−C stretching	12	3000	0.12	0.98
H−C−H bending	4	1440	1.16	3.22
H−C−C bending	18	950	13.27	23.67
C−C stretching	2	1000	1.34	2.52
C⋮⋮C stretching	4	1335	1.45	3.62
C−C−C bending	2	320	5.14	3.78
C−C⋮⋮C bending	2	320	5.14	3.78
C⋮⋮C⋮⋮C bending	2	336	4.95	3.77
C⋮⋮C torsions	2	190	7.2	3.90
C⋮⋮C torsions	2	407	4.24	3.68
	50		44.0	52.92

coinciding with the adjacent carbon atoms for the purpose of rotational entropy calculation. Considering all these approximations it is still rather unlikely that the product of the moments of inertia is wrong by as much as a factor of four but such an error would change the frequency factor only by two.

Internal rotations around the bonds 3–4 and 5–6 are probably hindered to the same extent as in propylene; hence their contributions to the entropy at 600° are substantially those of free rotations. The rotation around the 4–5 bond, however, will be considered as hindered to the same extent as the internal rotations in propane; Pitzer's tables show that 0.8 E.U. should be deducted from the entropy of a corresponding free rotator, while the heat capacity is found equal to 2.1 cal. mole degree. It is possible, however, that because bond 4–5 is the reacting one, it is rather extended in the critical complex and therefore the rotation is more nearly free. If this is the case, the above entropy deduction should be wholly or partially eliminated and as much as 1.1 cal. should be deducted from the heat capacity of the complex.

Table IV gives the assumed vibrational frequencies of the complex, together with their entropy and heat capacity contributions. The bending frequency of the 1,2,3 and 6,7,8 carbon atoms was taken as the mean of the corresponding frequencies in allene[18] and propane.[15] The torsional frequencies of bonds 1–2, 2–3, 6–7, 7–8 were computed from Pitzer's values, allowing for a force constant one-half as large as that of a double bond. The symmetry factor of the activated complex was taken equal to two. The complex has two unpaired electrons; they probably combine to form the singlet and triplet states, but because of the large distance between the electrons the energy separations between these four states should be quite small. The electronic multiplicity was therefore taken care of by introducing a degeneracy factor of four. Adding together the various entropy and heat capacity contributions, the following are found for 600° and one mole per cc concentration:

$$S_{600°}=S_{tr}+S_{rot}+S_{vibr}+R\ln 4/2$$
$$=22.3+50.0+44.0+1.4=117.7\ \text{E.U.}$$
$$C_{v\,600°}=63.2\ \text{cal./mole degree.}$$

Neither entropy nor heat capacity include the translational contributions of the reacting bond 4–5. Hence $\Delta S^*=S^*-2S_B=17.1$ E.U.

Substitution of this value into Eq. (7) gives for the frequency factor A the result:

calculated $A_{600°}=10^{10.27}$; observed $A_{600°}=10^{9.96}$.

It is somewhat difficult to estimate the errors involved in our calculation but five E.U. seems a reasonable value, considering the agreement which Pitzer, whose procedure we have substantially adopted, is able to obtain at lower temperatures and for simpler molecules. Hence the calculated rate constant is uncertain by a factor of ten and the agreement of calculation and experiment is seen to be excellent.

The experimental data presented in Table II suggest an increase of activation energy with temperature. The statistical calculations bear this out; the molar heat capacity of the activated complex excluding the reacting degree of freedom is 4.2 cal./degree greater than that of two moles of butadiene. To take account of this and of the kT/h factor in the statistical rate expression, 3 ln T must be introduced into the empirical Eq. (4). This improves still further the agreement between calculated and observed rate constants of Table II.

(III) Cyclic complex

We shall now consider a cyclic activated complex. Unfortunately the knowledge of vibrational frequencies in aliphatic rings is very imper-

[18] J. W. Linnett and W. H. Avery, J. Chem. Phys. **6**, 686 (1938).

fect and it would be fruitless to adopt the procedure made use of above. However, it is possible to estimate the entropy of vinyl cyclohexene at 298°K starting from entropies of related compounds and correcting them by amounts which characterize analogous structural changes in other homologous series.

Starting with values given by Parks and Huffman[19] for the liquid state, calculations of the entropy in the standard vapor state were made. Heats of vaporization at the boiling points were taken from Bennewitz and Rossner[20] or were found by means of the Bingham-Trouton Rule. They were converted to 298°K by the equation: $\Delta H_{298}=\Delta H_b+4(T_b-298)$. The vapor pressures at 298° were taken from Parks and Huffman or found with the aid of the Clapeyron-Clausius equation.

These values were corrected to give approximate entropies of 3-vinyl cyclohexene by various combinations of the following:

Replacement of a single bond by a double bond;

$\Delta S=$ (*cis*-2-butene) − (*n*-butane) = −1.5 E.U.

Introduction of a CH_2=group;

$\Delta S=$ (butene-1) − (propane) = +10.6.

Introduction of a $-CH_2-$ group;

$\Delta S=$ (*n*-butane) − (propane) = 10.3.

Addition of a vinyl side chain;

$\Delta S=$ (butene-1) − (ethane + R ln 18) = 14.8.

Results are shown in Table V and are seen to be reasonably self-consistent. The largest value was taken for the following calculations. Bennewitz and Rossner[20] have proposed an empirical rule for the calculation of gaseous heat capacities, which seems to give very satisfactory agreement with experimental data. Their procedure was used in calculating the heat capacity of vinyl cyclohexene at 450°K, 47.0 cal./mole degree being obtained. Treating this as a constant, one obtains 32.7 E.U. increase in entropy for the 298–600°K temperature interval. Conversion to moles/cc as units gives the entropy of vinyl cyclohexene at 600° as 101.5 E.U. Substitution of this into Eq. (7) results in a frequency factor equal to $10^{6.7}$. It differs from the experimental one by $10^{3.3}$. Since the entropy of the reacting degree of freedom was counted twice—once as vibration of the ordinary vinyl cyclohexene molecule and then once again in the kT/h factor of the statistical equation—the true discrepancy may be even slightly larger, unless, of course, the critical complex has a much looser structure than the ordinary vinyl cyclohexene molecule. This would have only a trifling effect upon the rotational entropy, but a half-dozen vibrational frequencies of about 150 cm^{-1} each would bring the calculation and experiment together.

The following objection must be raised, however; loose structure of the activated complex requires large interatomic distances, low force constants and hence small binding energies in its reacting degrees of freedom. In the process of formation of the cyclic molecule out of two butadienes three double bonds open to single ones to form eventually two new single and one double bond. Some 24 kcal. activation energy are available and yet the opening of a double bond requires probably not less than 55 kcal. energy. Hence the new bonds must become strong before the old ones weaken considerably and the activated complex, whatever its structure, cannot be very loosely held together.

(IV) Dissociation of dimer

The knowledge of the entropies of vinyl cyclohexene and of the intermediary free radical enable one to calculate the rate of dissociation of the former. The resulting expression should be valid at least in that temperature and concentration range which has been studied in dimerization reactions, because here at any rate the same activated complex must control both opposed rates to yield a thermodynamically correct equilibrium expression. The dissociation of vinyl cyclohexene must be thought of, therefore, as a

TABLE V. *Estimates of the entropy of 3-vinyl cyclohexene at 298° K and one atmosphere.*

Starting from	
cyclohexane	89.6 E.U.
methyl cyclohexane	90.3
cyclohexene	88.3
ethyl cyclohexane	86.7

[19] G. S. Parks and H. M. Huffman, *Free Energies of Some Organic Compounds* (Chemical Catalogue Co., New York, 1932).

[20] K. Bennewitz and W. Rossner, Zeits. f. physik Chemie **B39**, 126 (1938).

rapidly established equilibrium with the free radical, accompanied by a slow decomposition of the latter. The statistical rate expression gives the following:

$$k_{diss} = 10^{16.6} \exp(-63{,}000/RT) \text{ sec.}^{-1}.$$

The activation energy is rather uncertain, having been calculated from the heat of the reaction discussed in the previous paper.

Dissociation of vinyl cyclohexene has not been studied, but Lacher measured the dissociation rate of endomethylenetetrahydrobenzaldehyde, the condensation product of cyclopentadiene and acrolein. His rate expression is $10^{12.3} \exp(-33{,}600/RT)$, rather significantly different from the one calculated above. However, allowing a 20-percent error in the rate constants of Lacher, a not impossible assumption, his rate expression receives the form $10^{15} \exp(-39{,}700/RT)$. Such frequency factor is about midway between the one given above for vinyl cyclohexene and the frequency factor of dicyclopentadiene dissociation.* Such gradation of frequency factors is to be expected because the complex in the dicyclopentadiene reaction has the ring structures of two cyclopentadiene molecules and hence lacks free rotations and some of the low vibrational frequencies responsible for the large entropy of the butadiene free radical. Lacher's compound, which decomposes to give one cyclopentadiene molecule, should therefore have an intermediate frequency factor.

(V) Other considerations

It was commented in the previous paper that condensations of aldehydes with dienes consistently have lower frequency factors (by about tenfold) than those of two diene molecules. A search for a plausible statistical explanation has not been wholly successful, but it may be pointed out that in the reaction of aldehydes one end of the free radical has the structure O⋯CH⋯CH– and hence lacks the low torsional frequency of the terminal CH_2 group of radicals formed from hydrocarbons. This may account for some, if not all, of the observed difference. It is not to be denied that some uncertainties still remain concerning the details of diene association but in the main we believe to have definitely established their mechanism.

In other reactions of the dienes the radicals of the type here discussed may also be involved The study of the pertinent literature reveals no evidence against the assumption that all 1,4 additions to dienes occur in steps rather than by a simultaneous addition to both carbon atoms as discussed for instance by Eyring.[21] Thus the mechanism for bromine addition may be as follows. The first step is the formation of a radical:

$$BrH_2C - \dot{C}H - CH = CH_2$$

which is stabilized by resonance to the extent of 15 kcal., according to Coulson, and should therefore be formed in preference to the radical

$$H_2\dot{C} - CHBr - CH = CH_2.$$

The resonating radical offers equal opportunities for further addition on carbon atoms 2 and 4, but because of steric hindrance one product may be formed almost exclusively.

* Harkness, Kistiakowsky and Mears, reference 1, give $A = 1 \times 10^{13}$; Benford, Khambata and Wassermann, reference 1, give $A = 1.3 \times 10^{13}$; König, reference 1, gives $A = 2 \times 10^{14}$; this seems to be the most reliable figure.

[21] Eyring, Sherman and Kimball, J. Chem. Phys. 1, 586 (1933).

Discussion

L. S. Kassel: I would like to know what geometrical picture was assumed for the polymerized butadiene molecule. I assume that it is not exactly linear.

J. C. Morris, *Harvard University:* Professor Kistiakowsky has shown by physical properties that it is the cyclic dimer.

F. O. Rice, *Catholic University of America:* In some work on butadiene I found products 75 percent of vinyl cyclohexene and 25 percent of something else.

J. C. Morris, *Harvard University:* Professor Kistiakowsky said that he was able to account for 99 percent of the product.

H. Gershinowitz, *Shell Oil Company:* I should like to ask Professor Rice at what temperature his butadiene polymer was prepared. Is there not a possibility that at high temperatures the double bond in the vinyl group might migrate into the ring to form ethyl cyclohexadiene?

F. O. Rice, *Catholic University of America:* We polymerized at 420–460°C and two atmospheres pressure, but used short contact times so that about two-thirds of the butadiene was recovered. We have not been able to devise any satisfactory mechanism for migration of the double bond into the ring in the gas phase.

L. S. Kassel: What bond angles were assumed for butadiene and its polymers?

J. C. Morris, *Harvard University:* Somewhere between the tetrahedral angle and 120°.

L. S. Kassel: The bond angle may change a little when a double bond is introduced, but the principal thing that happens is a definite, fixed orientation of the other bonds. With the single bond there is a choice of three positions. There are four bonds, the character of which would be affected by the two structures. The space configuration would depend very much on the bond angles.

Kinetics of the Vapor Phase Reaction of Cyclopropane with Iodine *

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The thermal and photoreaction (light absorbed by iodine) between gaseous iodine and cyclopropane has been studied, and found to lead to the reversible formation of 1,3 diiodopropane. A slow iodine catalyzed isomerization of cyclopropane to propylene is the only important side reaction. The reaction is essentially homogeneous. For the thermal reaction, in the range 245–280°C, the rate expression is

$$\frac{d(C_3H_6I_2)}{dt}=k_1\left[(C_3H_6)(I_2)^{\frac{1}{2}}-K_e\frac{(C_3H_6I_2)}{(I_2)^{\frac{1}{2}}}\right].$$

For the photoreaction, in the range 180–230°C, the rate expression is

$$d(C_3H_6I_2)/dt=k_3I_{abs}{}^{\frac{1}{2}}(C_3H_6).$$

The respective values of k_1 and k_3 were found to be

$$1.17\times10^{13}e^{-35,230/RT}(\text{mole/cc})^{-\frac{1}{2}}\text{ sec.}^{-1}$$

and

$$8.5\times10^{6}e^{-18,800/RT}(\text{Einstein/cc})^{-\frac{1}{2}}\text{ sec.}^{-\frac{1}{2}}.$$

The mechanism has been established, the rate determining step being the reaction $I+C_3H_6\rightarrow ICH_2CH_2CH_2$, with rate constant

$$7.36\times10^{12}e^{-17,280/RT}(\text{mole/cc})^{-1}\text{ sec.}^{-1}.$$

The equilibrium constant, K_e, in the temperature range 255°–280°C, is some

$$11.7e^{-17,200/RT}(\text{mole/cc}).$$

Hence for the reaction $C_3H_6+I_2\rightarrow C_3H_6I_2$, $\Delta E=-17{,}200$ calories per mole. If the energy of the carbon-iodine linkages is taken as 43,000 calories, that of the carbon-carbon linkage in the cyclopropane ring is 32,900 calories per mole.

WHILE it is familiar knowledge to organic chemists that a number of reagents cause ring opening in cyclopropane and its derivatives, there is as yet little evidence bearing upon the mechanism of such reactions. The kinetic studies here reported were undertaken in order to remedy this deficiency in part. The reaction chosen for investigation was that between gaseous cyclopropane and iodine, which is shown below to lead to the reversible formation of 1,3 diiodopropane. This reaction was first observed by the authors, and reported briefly in a previous communication.[1] The present work deals with further qualitative evidence demonstrating the suitability of the reaction for kinetic study, and with the results of the quantitative studies of rates and equilibrium.

MATERIALS

Cyclopropane was obtained from the Ohio Chemical and Manufacturing Company. The purity, on the basis of absorption in fuming sulfuric acid, was 99.4 percent; the boiling range was −34° to −30°. The substance was used without further purification. Suitable portions were distilled from the cylinder into a trap (cooled with acetone—"dry ice" mixture) connected through a stopcock to the gas line. Samples were thoroughly outgassed (using liquid air for cooling) prior to each experiment.

Iodine was purified by sublimation from an intimate mixture with dry potassium iodide. It was then melted and stored over a drying agent.

1,3 diiodopropane was synthesized from iodine and cyclopropane (i.e., by the reaction with which this study is concerned). After each of the rate experiments (below) the gases were condensed in a removable side-arm. Warming the contents caused volatilization of the cyclo-

* Presented at the symposium on "Kinetics of Homogeneous Gas Reactions." See page 725.

** Holder of the E. I. duPont de Nemours Fellowship in Chemistry.

[1] R. A. Ogg, Jr., and W. J. Priest, J. Am. Chem. Soc. 60, 217 (1938).

propane and propylene, leaving a liquid mixture of iodine and 1,3 diiodopropane. The aggregate of samples from a large number of experiments, together with an excess of mercury (to remove iodine) was introduced into one limb of a small two-legged tube attached to the gas line. After thorough evacuation the tube was sealed off. The 1,3 diiodopropane was then slowly distilled into the other leg (cooled in an acetone-"dry ice" bath), appearing as a colorless, oily liquid. Its identity and purity are discussed below. The sample proved remarkably stable, showing no discoloration on very long standing.

Analytical Methods

To follow the isomerization reported below, a microanalytical method for gaseous cyclopropane-propylene mixtures was necessary. An adaptation of the procedure of Blacet and Leighton[2] proved satisfactory. A saturated aqueous solution of silver nitrate, retained in a sintered glass bead, was found to be a suitable absorbent for propylene, whereas it was without effect on cyclopropane (at least for periods of a few hours). Samples for analysis were exposed to the reagent for a period of some 40 minutes, and then dried by means of a fused potassium hydroxide bead. Analysis of cyclopropane-propylene mixtures of known composition indicated the results of this method to be accurate within one percent. Both propylene and cyclopropane were found to be rapidly and completely absorbed by fuming sulfuric acid—a reaction distinguishing them from saturated hydrocarbons, hydrogen, etc.

The gas samples to be analyzed were obtained in small bulbs, some five cc in volume, with two slender, fragile side arms. By immersing the bulb and the inverted sample cup[2] under a mercury surface, and breaking the side arms in succession, the gas sample was transferred to the cup.

Microanalysis of the 1,3 diiodopropane for iodine was performed as follows. A weighed sample was dissolved in liquid ammonia, to which bits of metallic sodium were then added until a permanent blue color resulted. After evaporation of the ammonia, the residue was dissolved in water and made slightly acidic with acetic acid. Iodide ion was then titrated with standard silver nitrate solution, potassium chromate indicator being used.

Qualitative Study of Cyclopropane-Iodine Reaction

As was mentioned in the previous communication,[1] the first observations of this reaction were based upon the disappearance of the characteristic iodine color in heated sealed bulbs containing iodine and excess cyclopropane. Complete disappearance of the iodine was never observed—a fact suggesting that the reaction is reversible. The contents of the bulbs, and in the quantitative experiments below, of the reaction vessel, were rapidly and completely condensed by liquid air—indicating the absence of appreciable quantities of hydrogen or low boiling hydrocarbons. No trace of hydrogen iodide could be detected on opening the bulbs.

The density and refractive index of the reaction product were found to agree[1] with values reported for 1,3 diiodopropane. The very small vapor pressure at room temperature is in accord with the reported boiling point of 227°. An analysis was performed as above.

Anal. Subs. 0.01748, 0.02083 g; 0.1000*N* $AgNO_3$, 1.19, 1.40 cc;
Calc. for $C_3H_6I_2$: *I*, 85.8%. Found: 86.4, 85.3%.

Hence the disappearance of the iodine is to be ascribed only to the reaction

$$C_3H_6+I_2\rightarrow IC_3H_6I.$$

The following experiment indicates the above reaction to be essentially reversible. A 125-cc sealed bulb containing 3×10^{-4} mole of $C_3H_6I_2$ was heated for 100 minutes at about 250°. Titration of the iodine produced indicated some 20 percent decomposition. The gas produced was found to contain less than one percent of propylene, and to be completely absorbable by fuming sulfuric acid.

That a relatively slow iodine catalyzed isomerization of cyclopropane to propylene accompanies the above reactions is indicated by the

[2] F. E. Blacet and P. A. Leighton, Analytical Edition, Ind. Eng. Chem. 3, 266 (1931). The authors wish to express their gratitude to Professor Leighton for loan of the necessary equipment, and for much helpful advice.

following experiments. A five-cc sealed bulb containing some 10^{-4} mole of $C_3H_6I_2$ was heated for 120 minutes at about 270°. Decomposition was more extensive than in the experiment described in the preceding paragraph and the final iodine concentration was of course much greater. The gas was found to contain 33.8 percent of propylene, the remainder being cyclopropane. The most striking experiment was performed with the apparatus used for the rate and equilibrium studies. A mixture of cyclopropane (93.2 mm pressure) and iodine vapor (86.6 mm) was maintained at a temperature of 279.2°. There was an initial pressure *decrease*, due to the reaction $C_3H_6+I_2\rightarrow C_3H_6I_2$. At the end of three hours the total pressure had reached a minimum value of 144.4 mm. A very slow *increase* in pressure then became noticeable, and at the end of eighteen hours the value of 177.5 mm had been reached—a figure only slightly less than the initial value. After condensation of the iodine, the gas was withdrawn for analysis. It proved to be essentially pure propylene.

From the rate expression (below) for the reaction $C_3H_6+I_2\rightarrow C_3H_6I_2$, the Law of Mass Action demands that the rate of the reverse reaction be an inverse function of iodine concentration. Since the apparatus described below did not permit a ready investigation of the rate of the reaction $C_3H_6I_2\rightarrow C_3H_6+I_2$, recourse was had to qualitative proof of this point. Into two Pyrex bulbs, each of 125-cc volume, were introduced, respectively, 2.94×10^{-4} mole of $C_3H_6I_2$ (bulb I) and 3.28×10^{-4} mole of $C_3H_6I_2$ and 2.554×10^{-4} mole of I_2 (bulb II). After evacuation the two bulbs were sealed off. They were heated simultaneously for 100 minutes in an air thermostat maintained at some 250°. After cooling the bulbs were opened and washed out with potassium iodide solution. The iodine was titrated with standard thiosulfate (Note that bulb II contained I_2 initially). *Analysis:*—Bulb I: 0.06735*M* $Na_2S_2O_3$, 1.66 cc; 20.0 percent decomposition; bulb II: 0.06735*M* $Na_2S_2O_3$, 8.35 cc; 7.2 percent decomposition. It is thus apparent that the addition of iodine produces a strong retardation of the decomposition of $C_3H_6I_2$. (Note that the initial concentrations of $C_3H_6I_2$ were nearly the same in the two, bulb II having the larger concentration.)

Apparatus and Procedure for Rate and Equilibrium Studies of Thermal Reaction

Pressure changes in a system of constant volume were used to follow the reaction, the substances involved being assumed to behave as *perfect gases*. The thermostat and quartz spiral manometer, temperature measurement, etc. were similar to those described in a previous communication.[3] The reaction vessel was a 500-cc Pyrex flask. Connection to the gas line (to which was attached the cyclopropane reservoir) was made successively through lagged and heated small bore tubing, two stopcocks (denoted as I and II) and a trap. The short glass line between the stopcocks was also lagged and heated, and in addition was provided with a small side arm, removable by means of a ground joint. This side arm and the stopcocks were furnished with removable heaters. Maintaining the heated sections at some 140° prevented condensation of $C_3H_6I_2$ and I_2. The stopcocks and ground joint were lubricated with a polymerized isobutylene, obtained through the courtesy of the Shell Development Company. This substance retains a satisfactory viscosity between room temperature and 140°, and proved relatively resistant to attack by iodine. The system was evacuated through a cold trap by a mercury diffusion pump.

For studies demonstrating the homogeneous character of the reaction, the flask was replaced by one filled with bits of broken Pyrex tubing. In this way the surface-volume ratio was increased some eleven-fold. Since fresh glass surfaces might conceivably have a slight catalytic activity, before rate measurements the packed flask was heated for some hours with cyclopropane-iodine mixtures. Air was never admitted to the hot flask between measurements.

The procedure of a typical rate measurement follows. The thermostat was brought to the desired temperature and the cell was thoroughly evacuated. Stopcock I was then closed, and the small side arm was removed. After introduction of an approximately known weight of solid iodine, it was replaced. After cooling the iodine, the space between stopcocks I and II was

[3] R. A. Ogg, Jr., J. Am. Chem. Soc. **56**, 526 (1934).

evacuated. Stopcock II was then closed, and the heater was slipped over the side arm, causing volatilization of the iodine. Stopcock I was opened until approximately the desired pressure of I_2 vapor was reached in the cell. This pressure was measured accurately. The iodine remaining in the space between the stopcocks was recondensed in the side arm. Stopcock II was then opened, and the line up to stopcock I was filled with cyclopropane at a pressure of about one atmosphere (by regulating the temperature of the liquid in the reservoir). Stopcock I was then briefly opened until the desired total pressure was reached in the flask. This pressure was accurately measured as soon as possible after closing the stopcock (normally a delay of some 30 seconds). The initial pressure of cyclopropane was thus obtained by difference. Pressure readings were then made at suitable measured time intervals. (Meanwhile the unused cyclopropane was recondensed in the reservoir.) When the reaction had been followed sufficiently far, the contents of the flask were condensed in the side arm, which was then removed and cleaned (after closing stopcock I).

The necessity of a very accurate measurement of the initial pressure of cyclopropane required the following procedure for the equilibrium studies. The thermostat was adjusted to a constant temperature of some 235°, at which the reaction is *extremely slow*. The above procedure of introducing the reagents and determining their partial pressures was followed. The temperature of the thermostat was then raised to the desired value, and the reaction mixture was maintained at this temperature for a period which was estimated to be sufficient for attainment of concentrations within two-tenths of one percent of the equilibrium values. (See below for this calculation.) The total pressure was then accurately measured. The initial partial pressures were calculated by use of the gas laws from the values measured at the lower temperature.

Whereas (in the temperature range employed) the isomerization of cyclopropane to propylene was too slow to affect the rate studies of 1,3 diiodopropane formation, in the relatively long periods required to attain equilibrium there was usually an appreciable decrease in cyclopropane concentration by this isomerization. Hence, after the final pressure measurement mentioned in the preceding paragraph, the $C_3H_6I_2$ and I_2 were condensed by cooling, and a sample of the volatile constituents was withdrawn for analysis of the cyclopropane-propylene ratio. The sample was condensed by liquid air in a suitable small bulb (see above) which was then sealed off. Duplicate or triplicate gas analyses were made.

Apparatus and Procedure for Rate Studies of Photochemical Reaction

The photochemical reaction was also followed by pressure changes. The vessel mentioned above was replaced by a small Pyrex cylindrical cell 6.5 cm in length and 3 cm in diameter, with a volume of 46 cc. This cell had plane polished windows, and was rigidly mounted with the axis coinciding with that of the windows in the thermostat (see drawing in reference 3). The light source was a 500-watt projection lamp, the *unfiltered* radiation from which produced a sufficiently large reaction rate. The intensity of light transmitted through the cell was measured by a Moll surface thermopile, in conjunction with a high sensitivity galvanometer, suitably damped. The order of the elements of the optical system was as follows: lamp, shutter, lens, thermostat window (of ordinary glass), lens, reaction cell, double lens, thermostat window, lens, water-filled glass cell (to absorb infra-red radiation), surface thermopile. To enable observation of possible intensity fluctuations of the light source during a given experiment, a second beam from the lamp was focused onto a photovoltaic cell connected to a direct-current microammeter. Ordinarily any fluctuations amounted to only a few percent. Desired intensity variations were produced by introduction into the optical system (next to the first thermostat window) of blackened wire screens of previously measured transmissivity.

A ballistic method of reading the galvanometer deflections satisfactorily corrected for drift in the null setting. Deflections were found to be proportional to the intensity (in the range employed) of radiation incident upon the thermopile. The thermopile-galvanometer system was calibrated by use of National Bureau of Standards radiation standards, employing the conventional technique. In estimating the energy absorbed in the reaction cell, correction was

made for the considerable reflection losses at the various interfaces between the lamp and the thermopile.

The statement in the previous communication[1] to the effect that intense visible light does not enhance the rate of reaction of cyclopropane with iodine was based upon very rough observations, and is definitely erroneous. In this investigation a marked photochemical reaction was found. It was studied in a temperature range from 60° lower than that employed for the studies of the thermal reaction. Under these conditions the thermal reaction was negligibly slow in comparison to that produced by the above source of visible light. Of the constituents of the reaction mixture, only iodine has an appreciable absorption in the spectral range emitted by the incandescent lamp and transmitted by the optical system.

Pressure and temperature measurements were complicated by a pronounced Budde effect. On exposure of a cyclopropane-iodine mixture to radiation from the lamp there was an almost immediate pressure *increase* (amounting to a few percent), followed by a continuous *decrease* as a result of the photochemical reaction. On interrupting the exposure there was a relatively rapid *decrease* of pressure (to a constant value). For purposes of rate measurement, it was assumed that the reaction mixture was at a temperature *higher* than that prevailing in the thermostat by an amount calculated on the basis of the gas law from the pressure decrease on interruption of the exposure. This temperature difference ordinarily amounted to five degrees or less. Since the radiant energy absorbed per unit time did not significantly change during the couse of an experiment, the slow pressure decrease during exposure provided a reliable index of concentration change of the reactants.

The procedure of a typical photochemical rate measurement follows. After adjustment of the thermostat to the desired temperature and evacuation of the cell, the lamp was turned on and allowed to burn a few minutes to attain equilibrium. The shutter was then opened and the galvanometer deflection was measured. After closing the shutter the reactants were introduced as described above. The shutter was then opened, and the galvanometer deflection was again determined. The difference of these two deflections was a measure of the light energy absorbed in the reaction cell. The reaction was followed by suitably timed pressure readings. At the conclusion the galvanometer deflection was again measured. The shutter was then closed and the pressure *decrease* (Budde effect) was observed. After evacuation of the cell the galvanometer deflection was again measured (to observe possible changes in the intensity of the lamp). Under the conditions employed in the rate studies the rate of radiant energy absorption at the beginning of an experiment was essentially identical with that at the end.

In experiments designed to test the possible effect of added chemically inert foreign gases, nitrogen or benzene vapor were employed. The reactants were introduced as above, and (after closing stopcock II) excess cyclopropane was recondensed in the reservoir. If nitrogen was to be used, the gas line was filled with the pure gas at atmospheric pressure. Brief opening of stopcock II admitted the desired quantity to the reaction cell without appreciable back diffusion of reactants. The total pressure was then measured. If benzene was used, a suitable quantity of liquid was introduced into the side arm between the stopcocks. After vaporization of the liquid by the heater, the procedure was the same as for nitrogen.

Experimental Results

Rate of thermal reaction

As was noted above, the rate of iodine catalyzed isomerization of cyclopropane to propylene may be sensibly neglected in comparison with the rate of synthesis of 1,3 diiodopropane. Hence a measured decrease in *total* pressure is numerically equal to the decrease in *partial* pressure of cyclopropane and iodine, respectively.

In the temperature range employed, the rate measurements conform best to the expression

$$d(C_3H_6I_2)/dt = k_1(C_3H_6)(I_2)^{\frac{1}{2}} - k_2(C_3H_6I_2)/(I_2)^{\frac{1}{2}}. \quad (1)$$

The first term on the right side represents the rate of synthesis of 1,3 diiodopropane, the second term the rate of the reverse reaction. In principle both k_1 and k_2 may be found from rate measure-

ments covering a wide range of concentrations. In practice the values of k_2 so obtained are subject to considerable uncertainty. That is, for a given value of k_1 the accuracy with which experimental rates conform to the above expression is relatively insensitive to the value assigned to k_2. A corresponding (although smaller) uncertainty in the value of k_1 is inevitable. To circumvent this difficulty, recourse was had to the fact that $k_2=k_1K_e$, where K_e is the equilibrium constant $K_e=(C_3H_6)_e(I_2)_e/(C_3H_6I_2)_e$. Therefore the rate expression becomes

$$d\frac{(C_3H_6I_3)}{dt}=k_1\left\{(C_3H_6)(I_2)^{\frac{1}{2}}-K_e\frac{(C_3H_6I_2)}{(I_2)^{\frac{1}{2}}}\right\}. \quad (2)$$

By use of the values of K_e determined in separate experiments (see below), the rate measurements may be used to obtain accurate values of k_1. Since use of the differential equation was not feasible, values of k_1 were calculated by use of the integrated form.

$$k_1=-\frac{2}{(t_2-t_1)h}\left\{g^{\frac{1}{2}}\left[\tan^{-1}\left(\frac{a-x}{g}\right)^{\frac{1}{2}}-\tan^{-1}\left(\frac{a-u}{g}\right)^{\frac{1}{2}}\right]-\frac{f}{2\sqrt{-f}}\ln\frac{f+(-f(a-x))^{\frac{1}{2}}}{f-(-f(a-x))^{\frac{1}{2}}}\cdot\frac{f-(-f(a-u))^{\frac{1}{2}}}{f+(-f(a-u))^{\frac{1}{2}}}\right\}, \quad (3)$$

where

$h=[(b-a+K_e)^2+4aK_e]$
$g=(b-a+K_e)/2+h/2$
$f=(b-a+K_e)/2-h/2$
$a=(I_2)$ when $t=0$
$u=(C_3H_6I_2)$ at time t_1
$a-u=(I_2)$ at time t_1
$x=(C_3H_6I_2)$ at time t_2
$a-x=(I_2)$ at time t_2
$b=(C_3H_6)$ when $t=0$
$b-u=(C_3H_6)$ at time t_1
$b-x=(C_3H_6)$ at time t_2
$u+x=(C_3H_6I_2)$ at time t_2.

At the start of an experiment the reaction was abnormally slow—an effect attributed to delay in mixing of the reactants by diffusion. For this reason the time t_1 was usually chosen corresponding to some ten percent approach toward equilibrium. Values of k_1 were calculated for various time intervals, all with the *same* initial time t_1. In Table I are presented the results of a typical experiment, which indicates the validity of the rate expression. It will be observed that there is no drift in the values of k_1, and that the fluctuations are not serious. Attempts to apply other rate expressions (respectively of zero, first, three-halves and second-order with respect to iodine concentration) yield values of the "constant" which show a systematic drift.

In Table II are summarized the results of all of the experiments dealing with the rate of the thermal reaction. The column headings P_{I_2} and $P_{C_3H_6}$ denote the *initial* partial pressures of iodine and cyclopropane, respectively. The values of K_e are obtained from the experimental data discussed in the following section. Values of k_1 are each the *average* of values corresponding to the various intervals during a given experiment.

At the lowest temperature, 244.9° two experiments were conducted in which the reaction vessel had been filled with broken tubing, thus increasing the surface-volume ratio some elevenfold. The respective partial pressures of iodine were 102.6 and 82.5 mm; of cyclopropane, 120.0 and 85.3 mm. The respective values of k_1 were found to be 1.87 and 1.79×10^{-2} (mole/cc)$^{-\frac{1}{2}}$sec.$^{-1}$, in satisfactory agreement with the values in Table II. This is taken as sufficient proof of the essentially homogeneous nature of the reaction.

It is seen from Table II that at each temperature the respective values of k_1 corresponding to experiments covering a wide range of initial concentrations are in satisfactory agreement and

TABLE I. *Data for rate experiment No. 35. Temperature 253.1°; initial pressure,* I_2, *64.0 mm,* C_3H_6, *171.7 mm.*

t SEC.	PRESS. $C_3H_6I_2$ MM Hg	$K_e\times10^7$ (MOLE/CC)	$k_1\times10^2$ (MOLE/CC)$^{-\frac{1}{2}}$ SEC.$^{-1}$
600	4.5	8.356	
1140	8.2		3.137
1620	11.3		3.010
2160	14.9		3.290
2712	17.5		3.130
3750	22.7		3.130
4380	25.6		3.137
4800	27.1		3.090
5460	29.6		3.080
		Av.	3.128

that deviations from the mean are random. This fact, together with the constancy of k_1 values during each experiment, provides convincing evidence for the validity of the assumed rate expression.

The plot of log k_1 against $1/T$ is shown in Fig. 1. The values corresponding to the four lower temperatures fall on a straight line, indicating the Arrhenius equation to be obeyed. The value for the highest temperature falls below this line. It will appear in the subsequent discussion that the temperature coefficient of the iodine catalyzed isomerization of cyclopropane to propylene is probably greater than that of 1,3 diiodopropane synthesis. Hence at the highest temperature it is probable that the rate of isomerization may not be entirely neglected. Further, at this temperature the correction for the rate of the reverse reaction is the largest. Appreciable disappearance of cyclopropane by isomerization introduces an uncertainty in this correction. For these reasons it appears legitimate to give less weight to the high temperature value of k_1, and to draw the line as shown. From the slope of this line the activation energy corresponding to k_1 is found to be 35,230 calories per mole. This figure may be uncertain by some ± 1000 calories.

If the straight line in Fig. 1 is taken as the most probable representation of k_1 as a function of temperature, $k_1 = 1.17 \times 10^{13}\ e^{-(35{,}230/RT)} \times (\text{mole/cc})^{-\frac{1}{2}}\ \text{sec}^{-1}$.

TABLE II. *Rate constants for thermal reaction.*

Ex. No.	T, °C	P_{I_2} mm Hg	$P_{C_3H_6}$ mm Hg	$K_e \times 10^6$ (mole/cc)	$k_1 \times 10^2$ (mole/cc)$^{-\frac{1}{2}}$ sec.$^{-1}$
10C	279.2	64.6	67.5	1.807	12.51
15		64.0	126.3		14.62
11		68.3	95.9		13.80
16		80.8	120.4		13.56
13		73.6	104.2		13.74
14		71.3	95.9		13.04
17		73.0	142.6		13.68
18		90.9	47.6		12.50
19		87.8	50.7		13.21
20		91.0	49.7		13.04
22		86.8	86.7		12.56
23		86.6	93.2		14.62
				Av.	13.41
44	270.2	75.5	172.7	1.610	10.13
45		160.1	68.4		9.39
46		126.7	89.9		9.26
47		130.2	172.1		9.90
48		109.5	106.0		9.61
				Av.	9.67
38	261.6	91.8	101.2	1.224	5.38
39		123.8	56.1		5.66
40		84.5	130.5		5.24
41		119.0	119.5		5.90
42		94.5	115.5		5.42
43		82.0	101.6		5.45
				Av.	5.51
32C	253.1	72.3	105.3	0.8356	2.920
34		108.1	54.7		3.033
35		64.0	171.7		3.128
36		124.6	106.5		3.400
37		111.7	123.1		3.080
				Av.	3.113
25	244.9	100.5	116.7	0.7245*	1.970
26		94.1	168.1		2.000
27		109.2	56.2		1.886
28		74.2	159.4		1.852
30		109.8	58.8		1.779
31		81.3	77.6		1.931
24		77.1	72.6		1.767
32		96.4	118.4		1.864
				Av.	1.880

* Extrapolated from values at higher temperatures. At 244.9° the reaction is too slow to allow convenient experimental determination of the equilibrium constant.

Equilibrium

An approximate estimate of the time required for a given cyclopropane-iodine mixture to attain essential equilibrium with 1,3 diiodopropane was made as follows. As was mentioned above, the pressure of a reaction mixture decreased to a minimum value and then slowly increased. By considering that the minimum pressure represented attainment of equilibrium, and that no isomerization had occurred, a very rough value of K_e could be calculated. From this value of K_e and the rate measurements an approximate value of k_1 was found. Then in the integrated form of the rate expression (Eq. (3)) the concentrations at time "t_2" were set equal to 99.8 percent of those calculated from the rough value of K_e. Using the above values of k_1 and K_e, the equation was then solved for the desired time interval. Times so found corresponded to the rising branch of the pressure-time curves, and varied from some two hours at the highest temperature to some sixteen hours at the lowest. In practice the reaction mixtures were allowed to stand longer than the estimated time before pressure measurement and analysis. It is probable that in each case there was reached a state experimentally indistinguishable from true equilibrium.

The experimental results are presented in Table III. The column headings P_{I_2} and $P_{C_3H_6}$ represent *initial* partial pressures. P_{Final} repre-

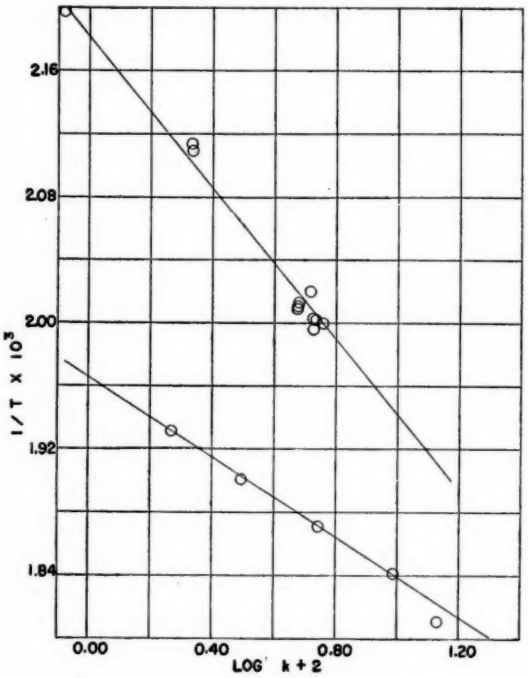

FIG. 1. Plots of log k_1 and log k_3 against $1/T$. Upper curve, k_3; lower curve, k_1.

sents the total pressure at "equilibrium." The sixth column gives the percentage of cyclopropane in the hydrocarbon fraction of the gases (the remainder being propylene).

Despite the fair agreement between duplicate values, no great accuracy can be claimed for the values of K_e. Fortunately the calculated values of k_1 (see above) are relatively insensitive to the value chosen for K_e. The plot of log K_e against $1/T$ in Fig. 2 indicates the large probable error in K_e. From the straight line which minimizes the square of the deviations it is found that $K_e = 11.7\ e^{-(17{,}200/RT)}$(mole/cc). Hence for the reaction $C_3H_6+I_2 \rightarrow C_3H_6I_2$, *the energy change*, $\Delta E = -17{,}200$ calories per mole. It is estimated that this figure may be in error by some ± 4000 calories.

Rate of photoreaction

In the temperature range employed, the measured rates of the photosynthesis of 1,3 diiodopropane were found to conform to the expression

$$d(C_3H_6I_2)/dt = k_3\, I_{abs}{}^{\frac{1}{2}}\, (C_3H_6). \qquad (4)$$

I_{abs} indicates the amount of radiant energy absorbed per unit volume per unit time. The reaction is thus of zero order with respect to iodine, which is the light absorbing component. By analogy with the rate expression for the thermal reaction, one might expect a second term corresponding to a photosensitized reverse reaction. However, it is apparent from the equilibrium studies that at the relatively low temperatures employed the equilibrium lies so far toward synthesis of 1,3 diiodopropane that correction for the reverse reaction is negligible (at least for moderate extent of reaction).

During a given experiment the factor I_{abs} remained essentially constant, despite the disappearance of iodine by the reaction. The reason is found in the spectral characteristics of the light source and the sharp decrease in absorption coefficient of iodine toward the red. Over the entire range of iodine concentrations used there was complete absorption (in the reaction cell) of the green and adjacent spectral regions, and nearly complete transmission of the red and infra-red.

With constant I_{abs}, the integrated form of the rate expression assumes the simple form

$$k_3 = \frac{1}{I_{abs}{}^{\frac{1}{2}}(t_2 - t_1)} \ln \frac{a}{a-x}, \qquad (5)$$

where "a" is the concentration of cyclopropane at time t_1, and $a-x$ the concentration at time t_2. For each experiment several values of k_3 were calculated corresponding to various time intervals, all with the same initial time (usually chosen a few minutes after the beginning of the experiment, to allow establishment of thermal equilibrium for the Budde effect). Table IV

TABLE III. *Equilibrium constants.*

Ex. No.	T, °C	P_{I_2} mm Hg	$P_{C_3H_6}$ mm Hg	P_{FINAL} mm Hg	% C_3H_6	$K_e \times 10^6$ (mole/cc)
E 1	279.2	75.9	135.1	181.7	86.9	1.798
E 2		69.5	115.4	160.9	87.2	1.815
					Av.	1.807
E 10	270.2	114.7	123.7	194.7	76.7	1.648
E 11		84.9	120.5	170.6	80.2	1.571
					Av.	1.610
E 9	261.6	74.2	97.3	138.9	84.2	1.326
E 12		97.0	153.0	194.5	80.2	1.122
					Av.	1.224
E 14	253.1	82.3	127.0	160.9	81.0	0.8240
E 15		88.2	154.3	183.9	85.6	0.8480
					Av.	0.8356

gives the results of a typical experiment. The temperature and pressure of cyclopropane are those obtaining in the *illuminated* zone as a result of the Budde effect. Values of k_3 in units of (Einstein/cc)$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$ are calculated on the basis of the assumption that the mean effective wave-length of absorbed light is 5000A (see below).

The deviations from the mean are more serious than in the case of the thermal reaction, but the absence of any trend in the values of k_3 indicates the validity of the rate expression (5). In Table V are summarized the results of all of the experiments. The column headings P_{I_2} and $P_{C_3H_6}$ refer to the respective *initial* partial pressures in the *illuminated* cell. The temperatures are estimated by the Budde effect (see discussion above). The values of k_3 are each the average of several values corresponding to different intervals in an experiment. Values of k_3 in units of (Einstein/cc)$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$ are calculated on the basis of the assumption that the mean wave-length of absorbed light is 5000A. This is almost exactly the wave-length of the maximum in the iodine absorption spectrum.[4] The fact that the intensity of the light source is greater on the long wave-length side (of 5000A) than on the short wave-length side is roughly balanced by a reversed trend in the absorption coefficients.

TABLE IV. *Data for rate experiment P 15. Temperature, 200°C; initial pressure, I_2, 44.4 mm, C_3H_6, 254.5 mm, I_{abs}, 1.78×10⁴ ergs per cc per sec.*

t_2-t_1 SEC.	x MM Hg	$k_3\times10^5$ (ERG/CC)$^{-\frac{1}{2}}$ SEC.$^{-\frac{1}{2}}$	$k_3\times10^2$ (EINSTEIN/CC)$^{-\frac{1}{2}}$ SEC.$^{-\frac{1}{2}}$
240	1.4	1.589	1.875
480	3.0	1.880	2.220
780	4.6	1.778	2.098
960	5.3	1.860	2.195
1200	7.7	1.907	2.250
1440	9.0	1.853	2.188
1680	10.5	1.888	2.228
1920	12.1	1.935	2.283
2160	13.1	1.848	2.177
2400	14.4	1.813	2.140
		Av. 1.840	Av. 2.170

TABLE V. *Rate constants for photoreaction.*

Ex. No.	T, °C	P_{I_2} MM Hg	$P_{C_3H_6}$ MM Hg	$I_{ABS}\times10^{-4}$ ERGS/CC SEC.$^{-1}$	$k_3\times10^5$ (ERG/CC)$^{-\frac{1}{2}}$ SEC.$^{-\frac{1}{2}}$	$k_3\times10^2$ (EINSTEIN/CC)$^{-\frac{1}{2}}$ SEC.$^{-\frac{1}{2}}$
P 23	228	98.0	95.0	1.76	4.44	5.30
P 7	228	120.6	69.1	3.12	4.57	5.39
P 8	228	108.8	132.5	2.99	4.45	5.25
P 6	227	52.7	144.0	2.37	4.84	5.72
P 19*	226.5	53.4	138.8	1.88	4.84	5.72
P 4	226.5	107.8	101.6	3.04	4.37	5.11
P 5	226	44.7	204.9	2.05	4.57	5.39
P 10	226	50.7	139.5	2.43	4.45	5.25
P 25†	226	54.2	151.4	1.71	3.06	3.61
P 11	225	53.6	159.8	0.803	3.98	4.69
P 12	224.5	73.6	208.1	0.872	3.98	4.69
P 9	223.5	61.1	200.1	0.822	4.06	4.78
P 13	222	57.2	251.1	0.145	4.29	5.06
P 14	222	61.4	139.3	0.140	4.57	5.39
P 16	201	65.0	148.0	2.10	1.85	2.18
P 15	200	44.4	254.5	1.78	1.84	2.17
P 18	182	82.9	226.8	2.33	0.748	0.882
P 20	182	58.8	231.8	1.91	0.721	0.850
P 21	182	75.7	247.9	2.20	0.685	0.808

* Added N_2 at partial pressure of 216.2 mm.
† Added C_6H_6 vapor at partial pressure of 536.5 mm.

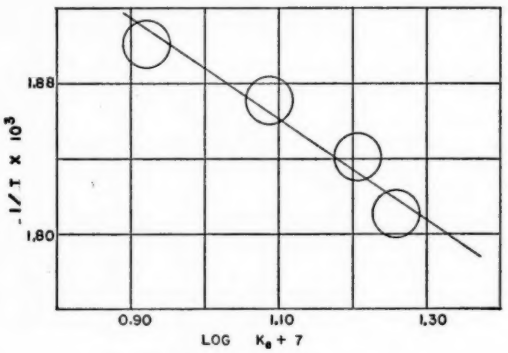

FIG. 2. Plot of K_e against $1/T$.

It will be observed that variation of I_{abs} by some twenty-five-fold leaves k_3 satisfactorily constant. Deviations of k_3 values from the mean are larger than in the case of the rate constant of the thermal reaction—the errors being ascribed chiefly to the Budde effect and thermal reaction. However, the accuracy of the *relative* values is quite sufficient to confirm the validity of the assumed rate expression. Due to possible systematic errors in the calibration of the thermopile-galvanometer system, it is doubtful that the *absolute* values of k_3 are reliable to within a factor of less than five.

It will appear in the discussion that k_3 should be an inverse function of the total concentration of gas molecules. Experiment *P* 25 indicates that the addition of benzene vapor at high pressure actually does *decrease* k_3. Experiment *P* 19 suggests that nitrogen is much less effective.

The plot of log k_3 against $1/T$ appears in Fig. 1. Deviations from the most probable straight line

[4] K. Vogt and R. Königsberger, Zeits. f. Physik 13, 300 (1923).

are ascribed to errors discussed above. From the equation of this line.

$$k_3 = 7.2e^{-18,800/RT}\left(\frac{\text{erg}}{\text{cc}}\right)^{-\frac{1}{2}} \text{sec.}^{-\frac{1}{2}}$$

$$\text{or} \quad 8.5\times10^{6}e^{-18,800/RT}\left(\frac{\text{Einstein}}{\text{cc}}\right)^{-\frac{1}{2}} \text{sec.}^{-\frac{1}{2}}.$$

The activation energy is thus 18,800 calories per mole for the photoreaction. The estimated error is ±2000 calories.

Discussion

The results concerning the rates of the thermal and photochemical synthesis of 1,3 diiodopropane are explained in terms of the following mechanism. "*M*" indicates any molecule capable of acting as a third body for atom recombination. The column on the right gives the corresponding rate constants. "I_{abs}" indicates the number of Einsteins absorbed per unit volume per unit time.

$I_2+h\nu\rightarrow 2I$	I_{abs}	(a)
$I_2+M\rightarrow 2I+M$	k_b	(b)
$2I+M\rightarrow I_2+M$	k_c	(c)
$I+C_3H_6\rightarrow ICH_2CH_2CH_2$	k_d	(d)
$ICH_2CH_2CH_2\rightarrow I+C_3H_6$	k_e	(e)
$ICH_2CH_2CH_2+I_2\rightarrow C_3H_6I_2+I$	k_f.	(f)

To obtain agreement with the empirical rate expressions, it must be assumed that the formation of the free radical $ICH_2CH_2CH_2$ is the rate controlling step, i.e., that $k_f(I_2)\gg k_e$. Application of the familiar steady-state treatment yields for the *thermal reaction*

$$\frac{d(C_3H_6I_2)}{dt} = k_d\left(\frac{k_b}{k_c}\right)^{\frac{1}{2}}(C_3H_6)(I_2)^{\frac{1}{2}} = k_dK_{I_2}{}^{\frac{1}{2}}(C_3H_6)(I_2)^{\frac{1}{2}},$$

where $K_{I_2}=(I)^2/(I_2)$, the dissociation constant of iodine. Comparison with the first term (corresponding to forward reaction) in the empirical Eq. (1) indicates that $k_1=k_dK_{I_2}{}^{\frac{1}{2}}$. From the data of Bodenstein and Starck[5] in the temperature range concerned

$$K_{I_2} = 2.53e^{-35,900/RT}\left(\frac{\text{mole}}{\text{cc}}\right).$$

Since

$$k_1 = 1.17\times10^{13}e^{-35,230/RT}\left(\frac{\text{mole}}{\text{cc}}\right)^{-\frac{1}{2}} \text{sec.}^{-1}$$

(see above),

$$k_d = 7.36\times10^{12}e^{-17,280/RT}\ (\text{mole/cc})^{-1}\ \text{sec.}^{-1}.$$

Application of the steady-state treatment yields for the *photoreaction*

$$d(C_3H_6I_2)/dt = k_d[k_c(M)]^{-\frac{1}{2}}I_{abs}{}^{\frac{1}{2}}(C_3H_6).$$

Comparison with the empirical Eq. (4) indicates that $k_3=k_d[k_c(M)]^{-\frac{1}{2}}$. The values of k_c have not been determined for iodine atom recombination with I_2, C_3H_6 or $C_3H_6I_2$ molecules acting as the third body, "*M*." However, the results of experiments *P* 19 and *P* 25 in Table V indicate that the molecules of the reaction mixture are much more effective than nitrogen and approximately as effective as benzene in reducing the value of k_3, i.e., in acting as the third body for iodine atom recombination. The values of k_c at room temperature for N_2 and C_6H_6 as third bodies were found by Rabinowitch and Wood[6] to be, respectively, 2.4×10^{16} and 3.5×10^{17} $(\text{mole/cc})^{-2}\ \text{sec.}^{-1}$. (Note that the present results are in qualitative agreement with the relative magnitude of these values.) It therefore appears legitimate to assume that for the molecules of the photochemical reaction mixture, the value of k_c is some 3.5×10^{17} $(\text{mole/cc})^{-2}\ \text{sec.}^{-1}$ i.e., the same as for benzene. (This also assumes k_c to be independent of temperature.) The average total pressure of the reaction mixtures was some 250 mm, at a mean temperature of some 200°C. This yields as an average value for (M) some 8.5×10^{-6} (mole/cc). Therefore the average value of $[k_c(M)]^{\frac{1}{2}}$ is found to be some 1.7×10^{6} $(\text{mole/cc})^{-\frac{1}{2}}\ \text{sec.}^{-1}$. Since from the experimental results $k_3=8.5\times10^{6}e^{-18,800/RT}$ $(\text{Einstein/cc})^{-\frac{1}{2}}$ $\text{sec.}^{-\frac{1}{2}}$ the calculated value of

$$k_d = 1.45\times10^{13}e^{-18,800/RT}\ (\text{mole/cc})^{-1}\ \text{sec.}^{-1}.$$

In view of the possible error in the experimental value of k_3, and the uncertainties in the

[5] M. Bodenstein and H. Starck, Zeits. f. Electrochem. **16**, 961 (1910).

[6] E. Rabinowitch and W. C. Wood, J. Chem. Phys. **4**, 497 (1936)

above calculation, the agreement between the values of k_d from the thermal and photoreactions is excellent, and constitutes the strongest proof of the validity of the assumed mechanism. It should be noted that the activation energies differ by only some 1500 calories—well within the estimated uncertainty of the activation energy for k_3—and that at a temperature of 500° absolute the respective numerical values of k_d differ by a factor of less than three. For subsequent considerations the value of k_d from the thermal reaction will be used, as it is considered more reliable than that from the photoreaction.

For application of *collision* theory of second-order reactions, the value of k_d may be expressed as $1.92\times10^{11}T^{\frac{1}{2}}e^{-(17,280-\frac{1}{2}RT)/RT}$ (mole/cc)$^{-1}$ sec.$^{-1}$. This corresponds to an "effective collision diameter" of 6.2×10^{-9} cm—an entirely plausible order of magnitude. For application of "*activated complex*" theory, k_d may be expressed as $2.81\times10^{14}T^{-\frac{1}{2}}e^{-(17,280+\frac{1}{2}RT)/RT}$ (mole/cc)$^{-1}$ sec.$^{-1}$. Assuming a "transmission coefficient" of unity, if only *translational entropy* were involved, the rate constant for reaction (d) should be $3.76\times10^{11}T^{-\frac{1}{2}}e^{-\Delta E_{Act}/RT}$ (mole/cc)$^{-1}$ sec.$^{-1}$. The difference corresponds to an *increase* of *vibrational* and *rotational* entropy of some 13.2 calories per degree in formation of the activated complex from I and C_3H_6. This figure seems entirely reasonable on physical grounds.

The rate of the *iodine catalyzed* decomposition of 1,2 diiodoethane into ethylene and iodine was found by Arnold and Kistiakowsky[7] to be proportional to $(C_2H_4I_2)(I_2)^{\frac{1}{2}}$. In consequence the rate of the synthesis must be proportional to $(C_2H_4)(I_2)^{\frac{1}{2}}$. This is explained by a mechanism very similar to that established above, but with the difference that the relative magnitudes of the rate constants corresponding to $k_f(I_2)$ and k_e is reversed. That is, for ethylene, *equilibrium* obtains for the reaction corresponding to (d), and the rate determining step is that corresponding to (f). It will appear that this reversal may be explained on the basis of the respective activation energies attending reaction (e) for ethylene and cyclopropane. The considerations are an extension of those previously advanced.[8]

[7] L. Arnold and G. B. Kistiakowsky, J. Chem. Phys. **1**, 166 (1933)

[8] R. A. Ogg, Jr., J. Am. Chem. Soc. **58**, 607 (1936).

It was shown[8] that for ethylene the constant corresponding to k_f was some $5\times10^{13}e^{-12,000/RT}$ (mole/cc)$^{-1}$ sec.$^{-1}$, and it is here assumed that for cyclopropane k_f is of the same magnitude. The concentration of iodine obtaining in the experiments was of the order of magnitude of 3×10^{-6} (mole/cc). At a temperature of 540° absolute (corresponding to the middle of the temperature range), the value of $k_f(I_2)\sim2\times10^3$ sec.$^{-1}$. It will be seen below that reaction (e) is probably *endothermic* by some 10,000 calories per mole. Since the activation energy of the reverse reaction (d) is some 17,200 calories, the activation energy of (e) is therefore 27,200 calories. If the "temperature independent factor" of k_e is assumed to be 10^{13} sec.$^{-1}$ (the usual magnitude for first-order rate constants), at 540°K $k_e\sim10^2$ sec.$^{-1}$. It is thus apparent that these numerical values satisfy the condition $k_f(I_2)\gg k_e$ established above. Even were the activation energy of reaction (f) negligible, this condition would require an activation energy of some 17,000 calories for (e). Thus apparently (e) cannot be exothermic.

1,2 diiodoethane also undergoes uncatalyzed decomposition.[7, 8] The fact that pure 1,3 diiodopropane decomposes on heating suggests a similar reaction, but it should be noted that the rate of decomposition by the above mechanism approaches infinity at vanishing iodine concentration. The strong retardation of this decomposition by added iodine is further evidence for the above mechanism.

Only qualitative inferences may be drawn concerning the rate of the iodine catalyzed isomerization of cyclopropane to propylene. It was noticed that the rough provisional "equilibrium constants" obtained from the minima in the pressure-time curves on the assumption of no isomerization approach more nearly to the true values the greater was the cyclopropane-iodine concentration ratio, and the lower the temperature. This suggests that the rate of isomerization is of *higher order* with respect to iodine concentration than is the rate of 1,3 diiodopropane formation, and that the activation energy is *greater* than for the latter reaction. The extents of isomerization in Table III bear out these points. By *assuming* the following reactions as an addition to the above mechanism, these facts may

be explained

$$ICH_2CH_2CH_2+I_2 \rightarrow ICH_2CHICH_3+I \quad (g)$$

$$ICH_2CHICH_3 \rightarrow I_2+CH_2=CH_2-CH_3 \text{ (Rapid)}. \quad (h)$$

Decomposition of ethylene diiodide is complete and extremely rapid[7] at the temperatures involved, and hence it seems legitimate to assume the same for propylene diiodide. The similarity of reaction (g) to that postulated in another investigation[9] should be noticed. There it was assumed that a *normal* propyl radical may react with an iodine molecule to yield *iso*-propyl iodide and iodine atom—i.e., with a concomitant shift of a hydrogen atom, just as in (g).

The equilibrium studies allow some interesting speculation. If it is *assumed* that the dissociation energy[3] of a carbon-iodine linkage in both $C_3H_6I_2$ and C_3H_6I is 43 kilocalories per mole, some reaction energies may be derived by use of Hess' Law.

Figures below are given in kilocalories per mole.

$C_3H_6+I_2 \rightarrow C_3H_6I_2$	$+17.2$
$2I \rightarrow I_2$	$+35.9$
$C_3H_6I_2 \rightarrow CH_2CH_2CH_2+2I$ (Assumed)	-86
$C_3H_6 \rightarrow CH_2CH_2CH_2$	-32.9

Likewise

$CH_2CH_2CH_2I \rightarrow CH_2CH_2CH_2+I$ (Assumed)	-43
$CH_2CH_2CH_2 \rightarrow C_3H_6$	$+32.9$
$CH_2CH_2CH_2I \rightarrow C_3H_6+I$	-10.1

The use of the energy change so found for reaction (e) in explaining the relative magnitudes of k_e and $k_f(I_2)$ (see above) may be taken as an independent check on the essential correctness of the assumed bond energy for the carbon-iodine link. If reaction (e) were assumed to be thermoneutral the dissociation energies of the carbon-iodine linkage and carbon-carbon linkage in cyclopropane would be found each as 52.9 kilocalories (an *upper* limit).

The figure 32.9 kilocalories seems rather small for the energy of a carbon-carbon linkage, but it must be borne in mind that the cyclopropane ring is highly strained. The activation energy for the first-order thermal isomerization of cyclopropane[10] is some 65 kilocalories. If the primary step is a fission of a carbon-carbon link, the "true" activation energy is some 32 kilocalories.

The equilibrium constant for the dissociation of 1,3 diiodopropane into cyclopropane and iodine was found above to be $11.7e^{-17,200/RT}$ (mole/cc). If only *translational* entropy change were involved, then from the familiar statistical equations, at 540°K the constant would be $8.5\times10^2e^{\Delta E/RT}$ (mole/cc). From the ratio of these two figures, at 540°K the *increase* in *rotational* and *vibrational* entropy in forming $C_3H_6I_2$ from C_3H_6 and I_2 is some 8.5 calories per degree. The great disparity between the masses of iodine atoms and those of carbon and hydrogen allows a simple interpretation of this change. To a first approximation any change in vibrational entropy will be neglected. Further, the molecule of 1,3 diiodopropane will be regarded essentially as diatomic, the moment of inertia being determined only by the separation of the iodine atoms. Finally, the rotational entropy of cyclopropane will be neglected (or rather taken as equal to the neglected contribution of the carbon and hydrogen atoms to the rotational entropy of 1,3 diiodopropane). The above entropy increase of 8.5 calories per degree thus arises principally from the increase in separation of the iodine atoms on forming 1,3 diiodopropane from iodine. Using the classical formula for the entropy of a rigid rotator, $S_{\text{Rot}}=R\ln(8\pi^2IkT/h^2)$, and an internuclear distance in iodine molecules of 2.66×10^{-8} cm, then at 540°K for iodine $S_{\text{Rot}}=18.4$ calories per degree. Hence at the same temperature for $C_3H_6I_2$, $S_{\text{Rot}}=18.4+8.5=26.9$ calories per degree. The calculated separation of iodine atoms in $C_3H_6I_2$, is then found to be 4.2×10^{-8} cm. This figure seems entirely reasonable on the basis of the geometrical structure and probable internuclear distances in $C_3H_6I_2$.

The authors wish to express their gratitude to Professor G. S. Parks, from whom was obtained the cyclopropane and polyisobutylene employed in this work. The work was made possible through the award by the duPont de Nemours Company of a fellowship to one of the authors (W. J. P.).

[9] J. L. Jones and R. A. Ogg, Jr., J. Am. Chem. Soc. **59**, 1931 (1937)

[10] T. S. Chambers and G. B. Kistiakowsky, J. Am. Chem. Soc. **56**, 399 (1939).

Discussion

R. A. Ogg, Jr., *Stanford University:* I wish to point out that the reaction $I+C_3H_6 \rightarrow ICH_2CH_2CH_2$ is most probably exothermic, and is at worst thermoneutral. Hence the measured activation energy of some 17 kilocalories is a "true" activation energy, corresponding to the height of a potential barrier. This is thus an addition to the steadily growing list of reactions of free atoms and radicals which are characterized by rather large true activation energies. It is significant that most of these involve hydrocarbon radicals, and suggests that the inertia of such radicals may result from an unexpected complexity in the state of the free valence electron.

The authors have also attempted the study of the bromine-cyclopropane reaction. While it does not share the chemically clean-cut character of the iodine reaction, the mechanism appears to be similar to that of the latter process. It is worthy of mention that the reaction $Br+C_3H_6 \rightarrow BrCH_2CH_2CH_2$ seems to have a much smaller activation energy than has the analogous iodine reaction. This is probably associated with the greater energy change for the bromine atom reaction.

D. C. Grahame, *University of California:* Is the 33-kcal. bond strength for C−C to be thought of as an average for the three bonds in cyclopropane or as a quantity characteristic of one bond only and independent of changes occurring simultaneously in the other two?

R. A. Ogg, Jr., *Stanford University:* The 33 kcal. is the strength of one highly strained C−C bond. The existence of the strain in cyclopropane becomes evident from the reaction itself. I_2 and normal propane do not react at these temperatures. This bond strength seems reasonable.

F. O. Rice, *Catholic University of America:* The large difference between the 33 kcal. and the value of Chambers and Kistiakowsky makes it desirable to obtain further confirmation for the mechanism proposed here.

How far did you vary the concentration of iodine with respect to that of cyclopropane? I ask this question because in experiments with low iodine concentration you might find a reaction in which the iodide decomposes to give ethylene.

R. A. Ogg, Jr., *Stanford University:* The light intensity in the photoreaction was varied over a twenty-five-fold range, equivalent to a fivefold variation in the steady-state concentration of iodine atoms.

No ethylene was found. We have studied the decomposition of pure 1, 3 di-iodopropane. No products other than cyclopropane, propylene and iodine were obtained. The possible alternative decomposition of the iodopropyl radical into hydrocarbon fragments would thus appear to be a negligible process.

Linus Pauling, *California Institute of Technology:* The value 33 kcal. subtracted from the normal carbon-carbon bond energy should give the strain energy. The normal value is usually given as near 60 kcal., and the strain is thus quite large. However, the heat of the reaction $C_3H_6+I_2 \rightarrow I(CH_2)_3I$ should give the total strain energy of the cyclopropane molecule directly. The mean of the C−C and I−I bonds should be quite near to the C−I bond strength, which would give zero heat of reaction for normal bonds. Since the measured value of this heat is 17 kcal., the strain energy for the C−C bond in cyclopropane should have about this value, which is reasonable.[11]

R. A. Ogg, Jr., *Stanford University:* I realize that the carbon-carbon bond energy obtained by this method seems rather low but it is difficult to see how simple calculations based on the law of Hess can be completely wrong.

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[11] The bond energy values given on page 53 of *The Nature of the Chemical Bond* (Cornell University Press, 1939), indicate a correction of 3.8 kcal. per mole which, with the measured heat of reaction leads to 21 kcal. per mole for the total strain energy of cyclopropane. This agrees well with the value of 24 kcal. per mole calculated from the heat of combustion.

The Experimental Basis for the Theory of Quasi-Unimolecular Reactions *

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Reactions which have been represented as of the quasi-unimolecular type are reviewed. With the possible exception of the isomerization of cyclopropane to propylene, it is suggested that no clean-cut examples have so far been discovered. In view of this conclusion it is further suggested that the apparent restriction placed on rate of activation by collision is in need of review.

IT HAS been apparent for some time that the experimental basis for the theory of quasi-unimolecular reactions was not altogether satisfactory. As individual examples have been more exhaustively investigated they have turned out to be "special cases," until it may be legitimately questioned whether the type of mechanism which the theory suggests has reality.

This is not to deny the logical difficulty involved. Even before a well-authenticated example of a first-order homogeneous gas reaction was available, Perrin and others[1] had pointed out that if such a reaction persisted to zero pressure, it must depend on environmental radiation for activation. Activation energy could not be supplied by a collision mechanism. Lindemann[2] then suggested that by providing for accumulation of activation energy in many degrees of freedom, and for a time-lag between activation and reaction, the first-order character could at least be preserved over a considerable pressure range. However, when calculations were made for the nitrogen pentoxide decomposition, which has become the classical example of a first-order gas reaction, it was evident that the observed maintenance of fractional rate to a few hundredths of a millimeter could perhaps just be accounted for.[3]

From the experimental standpoint the situation was temporarily saved by Hinshelwood's discovery that a number of organic decompositions appeared to be first-order reactions at about one atmos., but that the first-order constants fell with the pressure approximately as predicted by Lindemann's theory.[4] However, almost immediately the case was seriously weakened by the suggestion of F. O. Rice[5] that the reactions in question were by no means simple, but were of the chain type. Perhaps the best evidence of this was supplied by Hinshelwood himself when he showed that in many instances, the reactions are subject to inhibition by nitric oxide.[6] Even in those cases where inhibition is not observed the analytical evidence for complexity is very strong.[7]

One point particularly stressed in the earlier work was that hydrogen was able in many cases to restore the high pressure rate when the reactant was in the low pressure region. Thus in the case of ethyl ether, for example, the rate (at 525°C) begins to fall rather rapidly below 200 mm. The presence of 300 mm of hydrogen lifts this rate to a value characteristic of about 400–500 mm of the reactant.[8] But it was later shown by Newitt and Vernon[9] that there was nothing unique about the rate at 400–500 mm pressure. Measurements up to 15 atmos. revealed a continuous increase in the first-order constant. The high pressure limit showed no signs of being attained, and certainly was not attained at 400–500 mm.

The nature of these reactions could easily be enlarged on. There is little question of their

* Presented at the symposium on "Kinetics of Homogeneous Gas Reactions." See page 725.

[1] See L. S. Kassel, *Kinetics of Homogeneous Gas Reactions* (Chemical Catalogue Company, New York, 1932), Appendix I.

[2] F. A. Lindemann, Trans. Faraday Soc. **17**, 598 (1922).

[3] Reference 1, Chapter X.

[4] C. N. Hinshelwood, *Kinetics of Chemical Change in Gaseous Systems*, third edition (Oxford University Press, Oxford, England, 1933), Chapter V.

[5] F. O. Rice, *The Aliphatic Free Radicals* (Johns Hopkins Press, Baltimore, Maryland, 1935).

[6] E.g., Ethyl ether, L. A. K. Staveley and C. N. Hinshelwood, Proc. Roy. Soc. London **A154**, 335 (1936).

[7] E.g., Azomethane, E. W. Riblett and L. C. Rubin, J. Am. Chem. Soc. **59**, 1537 (1937).

[8] C. N. Hinshelwood, Proc. Roy. Soc. London **A114**, 84 (1927).

[9] D. M. Newitt and M. A. Vernon, Proc. Roy. Soc. London **A135**, 307 (1932).

complexity, however. Certainly it would be difficult at the present time to insist that any such gave incontrovertible evidence confirmatory of the Lindemann theory.

Another reaction which has been interpreted in these terms is the nitrous oxide decomposition. This reaction has had a curious history. Hinshelwood and Burk[10] originally concluded that the reaction was second order, and that the data were consistent with bimolecular collision reaction theory. They noted, however, that the second-order constants rose as reaction proceeded, indicating that the true order was lower, or that there was catalysis by products, or both. It was later shown by Volmer[11] that the increase of rate with initial pressure was more in harmony with quasi-unimolecular than with bimolecular reaction theory. In fact there was indication of an approach to constancy in fractional rate at 10 atmos. It was also shown that the rate was increased by inert gases.[12] Hunter[13] subsequently carried the measurements to 40 atmos. and found that the fractional rate continued to increase beyond 10 atmos., but once again at the highest pressures there appeared to be an approach to constancy. Nevertheless, it is also stated that explosions occurred when measurements at 70 atmos. were attempted. From these results and those of Musgrave and Hinshelwood[14] at lower pressures it was concluded that the decomposition of this simple molecule involved ". . . three separate quasi-unimolecular reactions which became independent of pressure at approximately 0.08, 5 and 30 atmos., respectively."

We may at once conclude that this reaction promises little of value as a direct test of the Lindemann theory. In fact it may be questioned whether the reaction is essentially of this type at all. If we accept that the primary step is unimolecular, there are two possibilities both of which produce atoms—

$$N_2O \rightarrow N_2+O \qquad (1)$$

$$N_2O \rightarrow NO+N. \qquad (1')$$

Given the production of atoms, there is then the possibility of a complex reaction of the chain type.

Suppose we consider (1′) as the primary reaction. This could be followed by—

[10] C. N. Hinshelwood and R. E. Burk, Proc. Roy. Soc. London **A106**, 284 (1924).

[11] M. Volmer and H. Kummerow, Zeits. f. physik. Chemie **9B**, 141 (1930); M. Volmer and N. Nagasako, *ibid.* **10B**, 414 (1930).

[12] M. Volmer, Zeits. f. physik. Chemie **21B**, 257 (1933); **25B**, 81 (1934); E. Lewis and C. N. Hinshelwood, Proc. Roy. Soc. London **A168**, 441 (1938).

[13] E. Hunter, Proc. Roy. Soc. London **A144**, 386 (1934).

[14] F. F. Musgrave and C. N. Hinshelwood, Proc. Roy. Soc. London **A144**, 386 (1934).

TABLE I. *Decomposition of nitrous oxide (Hunter). Time in seconds, pressure in kg/cm².*

857.8° ABS.				875.0°K				887.7°K			
TIME	p_{N_2O}	$k_1\times10^4$	$k_{1.5}\times10^5$	TIME	p_{N_2O}	$k_1\times10^4$	$k_{1.5}\times10^5$	TIME	p_{N_2O}	$k_1\times10^4$	$k_{1.5}\times10^5$
0	37.43			0	18.37			0	24.54		
		1.6	1.3			2.5	3.0			4.8	4.9
383	35.23			450	16.41			166	22.68		
		1.7	1.5			2.4	3.1			4.7	5.1
700	33.41			996	14.39			350	20.78		
		1.5	1.3			2.5	3.4			4.0	4.5
1135	31.29			1590	12.39			640	18.50		
		1.5	1.4			2.3	3.4			4.3	5.1
1590	29.21			2340	10.45			865	16.80		
		2.0	1.9			2.2	3.5			4.0	5.0
1990	27.00			3360	8.39			1185	14.80		
		1.5	1.5							3.7	5.1
2507	25.00							1645	12.46		
		1.5	1.5								
3068	23.00										
		1.2	1.3								
3760	21.11										
		1.4	1.5								
4460	19.19										

$$N+N_2O\rightarrow N_2+NO \quad (2)$$

$$NO+N_2O\rightarrow N_2+O_2+N \quad (3)$$

$$N+NO\rightarrow N_2O. \quad (4)$$

A steady-state solution gives

$$-d[N_2O]/dt=(k_1'k_2k_3/k_4)^{\frac{1}{2}}[N_2O]^{1.5}.$$

The reaction would then be of intermediate order. There is involved the constancy of $k_{1.5}$ as calculated in individual runs. Values obtained from Hunter's data (Table I) hardly allow a choice between k_1 and $k_{1.5}$, but are at least not unfavorable as to constancy. For the variation of $t_{\frac{1}{2}}$ (in terms of which most data are expressed) one obtains

$$t_{\frac{1}{2}}=0.4142/k_{1.5}p_0^{0.5}.$$

Thus a plot of log $t_{\frac{1}{2}}$ against log p_0 should show a slope of $\frac{1}{2}$. Reference to Fig. 1 shows that this is rather well fulfilled for Hunter's high pressure data.

Finally we may note that Musgrave and Hinshelwood[14] have shown that nitric oxide is produced up to a limited (steady-state) concentration and that this substance catalyses the reaction.

Another group of reactions which has been interpreted in terms of the Lindemann theory comprises certain isomerizations studied by Kistiakowsky. Of these, the *cis-trans*-isomerization reaction—

iso-stilbene→stilbene

appears to be a straight-forward first-order reaction, the constant of which is maintained at least between 4 and 3600 mm.[15] Essentially the same is true of the *cis-trans*-isomerization of methyl cinnamate, though here it is just possible that the first-order constant begins to fall below five mm pressure.[16] Thus neither of these reactions gives any certain evidence of being of the quasi-unimolecular type.

Two other *cis-trans*-isomerization reactions are very different from the above kinetically. These are the reactions—

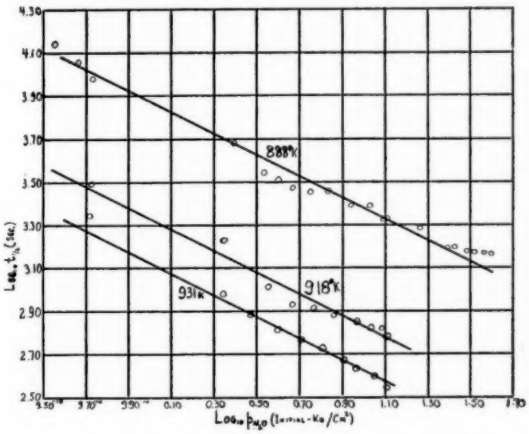

FIG. 1. Plot of log $t_{\frac{1}{2}}$ against log p_{N_2O}. (Hunter's data.)

methyl maleate→methyl fumarate[17]

cis-butene-2→*trans*-butene-2.[18]

In both cases, first-order constants fall as the initial pressure is decreased over the ranges studied, though there is some evidence of an approach to constancy at the highest pressures (4000 mm and 1500 mm, respectively). At any one pressure the constants appear to increase as reaction proceeds. The reaction kinetics are puzzling from any point of view. The rates are of the same order as for isostilbene and methyl cinnamate, but the temperature coefficients, and therefore the activation energies, are much less. This means that the A-factors in the equation—

$$k_1=Ae^{-E/kT}$$

are also much less. They are in fact so much smaller (order of 10^5 and unity, respectively) as to render meaningless the application of the Lindemann theory. The whole point of activation in many degrees of freedom was to obtain a sufficiently large rate of activation to accommodate high first-order rates (A of the order of $10^{10}-10^{15}$). In the cases under discussion the rates are far less than would correspond even to simple collision theory ($A\sim10^9$ for "normal" concentration, corresponding to 0°C and one atmos.). Whatever may be the explanation of the

[15] G. B. Kistiakowsky and W. R. Smith, J. Am. Chem. Soc. **56**, 638 (1934).

[16] G. B. Kistiakowsky and W. R. Smith, J. Am. Chem. Soc. **57**, 269 (1935).

[17] G. B. Kistiakowsky and M. Nelles, Zeits. f. physik. Chemie, *Bodenstein Fest-band* (1931), p. 369; J. Am. Chem. Soc. **54**, 2208 (1932).

[18] G. B. Kistiakowsky and W. R. Smith, J. Am. Chem. Soc. **58**, 766 (1936).

low rates, the reactions are certainly not ideal as experimental confirmations of the Lindemann theory.

There remains the isomerization of cyclopropane to propylene. This has been studied by Trautz and Winkler[19] and more completely by Chambers and Kistiakowsky.[20] There is agreement that the reaction is first-order and homogeneous. In addition, the latter authors report that the first-order constant falls slowly as the initial pressure is decreased from 700 to 10 mm, and that the results conform to Kassel's modification of the Lindemann theory.[21] This reaction therefore gives promise of being of the required type. It will be desirable, however, to await a more exhaustive investigation in view of the history of related studies.

Pending such an investigation or the discovery of new cases, it would appear that the Lindemann theory lacks a suitable experimental example. Admittedly, the logical difficulty about first-order reactions remains. A pressure will eventually be reached below which energy exchanges between molecules are too infrequent to support the high pressure equilibrium concentration of active molecules. It is nevertheless possible that in requiring mechanical contact at kinetic theory diameters we have placed an unnecessary restriction on the exchange. Certainly it is difficult to see how the nitrogen pentoxide case can be made consistent with such a restriction, especially if the observed decrease in rate at the lowest pressures turns out to be in part due to failure of the bimolecular reaction—

$$NO+N_2O_5\rightarrow 3NO_2,$$

as Daniels has suggested.[22]

Absorption and emission of energy by isolated molecules are subject to severe restrictions. In contrast, energy exchanges between the internal degrees of freedom of molecules in actual collision are granted very considerable latitude. In view of our uncertainty as to what constitutes actual collision for the latter purpose, one may imagine that the two extreme types of energy transfer run continuously into one another. Thus there is always a probability that emission by one molecule and absorption by another will occur. This probability becomes virtually a certainty in a kinetic theory collision. If the probability is a continuous function of the distance separating the two molecules, and presumably also of the amount of energy involved, the required increase in rate of activation would result. Until possibilities of this kind have been exhausted, it would seem unwise to be too dogmatic about the lower limit in first-order reactions. This attitude is so much the more reasonable, if in actual fact reactions of the required type are rare or nonexistent.

[19] M. Trautz and K. Winkler, J. prakt. Chemie [2] **104**, 53 (1922).
[20] T. S. Chambers and G. B. Kistiakowsky, J. Am. Chem. Soc. **56**, 299 (1934).
[21] L. S. Kassel, J. Phys. Chem. **32**, 235 (1928).
[22] F. Daniels, *Chemical Kinetics* (Cornell University Press, Ithaca, 1938), p. 71.

Discussion

R. N. Pease, *Princeton University:* It may be of interest to discuss in a little detail the possible alternatives to the quasi-unimolecular mechanism if the reaction is of the chain type. One may have an energy chain as suggested by Christiansen and Kramers,[24] with consequent multiplication of heat rate as compared to the primary unimolecular process. Again one may have an alteration in the kinetics of the reaction as the pressure is decreased, due to a change in the chain-ending process. This is implied in the Rice and Herzfeld treatment of the dimethyl ether decomposition[25] where it is pointed out that if the chain-ending reaction is $CH_3+CH_2OCH_3\rightarrow C_2H_5OCH_3$ the reaction will be first order. This is presumed to be the case at high pressures. At low pressures, the process is taken to be

$$2CH_3\rightarrow C_2H_6.$$

The over-all reaction would then be of 1.5 order.

One could write in general:

$$A\rightarrow R_1+R_2 \quad (1)$$

$$R_1\rightarrow R_2+\text{Product} \quad (2)$$

$$R_2+A\rightarrow R_1+\text{Product} \quad (3)$$

[24] Christiansen and Kramers, Zeits. f. physik. Chemie **104**, 451 (1923).
[25] Rice and Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934).

At the higher pressures the final chain-ending reaction is

$$R_1+R_2\rightarrow X \qquad (4)$$

and the reaction is first order. This demands that R_1 and R_2 be in substantially equal concentrations. But as the pressure of reactant A is decreased reaction (3) becomes less favorable, and the concentration of R_2 increases relative to R_1. Then the last stage might be

$$2R_2\rightarrow X \qquad (5)$$

corresponding to an over-all order of 1.5. Finally, at the lowest pressures one might have the loss of R_2 mainly at the walls, the reaction being

$$R_2+\text{wall}\rightarrow X. \qquad (6)$$

The over-all reaction would then be of second order. One can see that with the decrease of pressure the reaction could pass smoothly from the first order through 1.5 order to second order.

L. S. Kassel: The generally skeptical attitude of Professor Pease's comments is very much needed in reaction kinetics. Nevertheless, one or two minor points are somewhat debatable. Thus the acceleration of the rate of the nitrous oxide decomposition by truly inert gases, under conditions where there is no surface effect, must be taken to indicate collisional activation in a quasi-unimolecular step, even though the entire reaction perhaps has some complex mechanism. Incidentally, the particular chain rather casually proposed by Pease requires critical examination, not only on thermochemical grounds, but also with regard to the mathematical analysis. The steady-state solution given is based on treatment of both N and NO as transient intermediates. This is certainly incorrect for NO, which accumulates as a reaction product. When only N is taken as transient, the kinetic consequences of Pease's mechanism are

$$-\frac{d[N_2O]}{dt}=2\frac{k_1k_2[N_2O]^2+k_2k_3[N_2O]^2[NO]}{k_2[N_2O]+k_4[NO]},$$

$$\frac{d[NO]}{dt}=2\frac{k_1k_2[N_2O]^2-k_3k_4[N_2O][NO]^2}{k_2[N_2O]+k_4[NO]}.$$

The initial rate then follows a first-order law, and the half-life no simple law. If it is accepted as true that NO must be a catalyst, and must accumulate, it follows that $k_2[N_2O]>k_4[NO]$, and this condition makes it hard for the apparent order to be much greater than unity under any conditions. It is thus very doubtful that the Pease mechanism can be defended.

O. K. Rice, *University of North Carolina:* In the case of nitrous oxide, helium and argon accelerate the reaction. Anyone will grant that they are inert gases and do not take part in the reaction. About the only explanation possible is that they are contributing to the activation. It is quite possible that there might be a chain decomposition of nitrous oxide which would predominate at high pressure and a quasi-unimolecular reaction which would predominate at low pressure thus explaining the effect of pressure.

Another case in which the effect of inert gases has been thoroughly investigated is the decomposition of azomethane. Dr. Sickman and I tried helium and nitrogen which are surely inert, and others which are probably inert. With any given mixture we ran experiments over a considerable range of pressures, and in the case of carbon dioxide we used a mixture in which the inert gas was in a ratio of as high as 50 to 1. The effect of the inert gas, including the pressure dependence, was exactly as predicted by the theory. Furthermore we know that, though the reaction is not as simple and clean cut as might be desired, there is in all probability no chain involved in this reaction. I feel that the decomposition of azomethane must still be counted as an example of a quasi-unimolecular reaction.

R. A. Ogg, Jr., *Stanford University:* Professor Pease has pointed out that isomerization reactions represent the most favorable types for testing collision theories of quasi-unimolecular reactions. We are at present engaged with a study of the isomerization of iso-cyanides to normal cyanides (i.e., nitriles). For the methyl and ethyl compounds the reactions are homogeneous and apparently first order at constant gas pressure. The first-order constants decrease with initial concentration in essentially the fashion

demanded by theory. The possibility of chain reactions may be ruled out unequivocally, in view of the relatively small activation energies, i.e., some 40,000 calories. The frequency factors are even larger than the normal value of some 10^{13} sec.$^{-1}$. These reactions would thus appear to be good examples of quasi-unimolecular processes whose behavior supports the previous collision theories.

E. P. Wigner, *Princeton University:* I wish to add to what Dr. Kassel and Professor O. K. Rice have said that there is another fact in connection with the N_2O dissociation experiments which allows a slightly more favorable interpretation of these experiments from the point of view of the theory than the one just presented by Professor Pease. I refer to the change of the activation energy with pressure, observed both by Hunter and by Lewis and Hinshelwood. According to the latter, the activation energy increases from 47.7 kcal. to 57.7 kcal. as the pressure is increased from 25 to 600 mm. Hunter finds an increase from 50.5 to 65 kcal. This indicates that at the temperatures at which these observations were made, two processes contribute to the reaction, one with a smaller heat of activation and a small frequency factor, and another with a larger heat of activation and a large frequency factor. At the temperatures at which the experiments were made, the latter process is prevalent at high pressures. It must be expected, however, that it becomes less and less significant as one lowers the temperature so that this reaction would obey the theory at about 800°K and below. It is not at all unexpected that two or more processes should play a role at higher temperatures.

The chain reaction proposed by Professor Pease would show a temperature dependence corresponding to a heat of activation of at least 65 kcal. This figure is arrived at by assuming no heat of activation for his reactions (2) and (3) in the exothermic direction. Otherwise the heat of activation of Professor Pease's chain is even larger. This chain could be the mechanism of the high pressure process but cannot be, of course, the mechanism of the low pressure process.

A puzzling aspect of the low pressure mechanism is the very small frequency factor. This is, according to Lewis and Hinshelwood's figures[23] only 1.5×10^{7}. Although the often discussed non-adiabatic nature of the reaction $N_2O\rightarrow N_2+O$ may be partly responsible for this, one is inclined to Lewis and Hinshelwood's view that this is not the only factor.

One may expect a region of unimolecular behavior with a very low frequency factor in small molecules if the energy exchange between different proper vibrations is small. Further work must show whether or not this has anything to do with the low frequency factor in this case.

For the time being, of course, we must agree with Professor Pease's statement that the theory of unimolecular reactions does not yet afford us a real understanding of this reaction.

R. N. Pease, *Princeton University:* I hate to drag in surface effects but it is a fact that Dr. Hibben investigated the decomposition of N_2O at low pressure and concluded that it was purely a surface reaction at a fraction of a mm. I am wondering whether the inert gases may perhaps act as blanketers for the wall, making the loss of chain carriers at the wall less easy and therefore increasing the radical concentration rather than increasing the rate of activation. I don't think that the curve of $\log t_{1/2}$ *vs.* $\log P_0$ means 1.5 order any more than it means first order, but it is conceivable that one has a loss of chain carriers at the wall impeded by an inert gas. I don't know how to make a proper test for wall effects. We spent nearly a year on normal butane, chasing down wall effects. One kind of glass may give a faster reaction in an unpacked vessel. There seems to be a fifty-fifty chance of getting a slower rather than a faster reaction by packing the vessel with the same glass.

L. S. Kassel: The important fact is that an

[23] If Lewis and Hinshelwood's suggestion of two reaction mechanisms is correct, the frequency factor for the low pressure mechanism must be calculated using the activation heat of this process. Doing this, one arrives at the above frequency factor which is even smaller than Volmer's. This assumes, of course, acceptance of Lewis and Hinshelwood's tentative suggestion of two mechanisms and is, as they pointed out, in contradiction to the lack of constancy of their k_1/b, emphasized on their p. 451.

effect of packing is not found under the same conditions where inert gas increases the rate. It is true that for nonbranching chain reactions, in which the chains stop and start at the wall, packing produces no effect, but for such reactions there is no inert gas effect either.

Frank Verhoek, *Ohio State University:* I should like to ask Professor Pease whether he attempts to explain the decomposition of acetaldehyde on this chain basis. This decomposition is not inhibited by nitric oxide.

R. N. Pease, *Princeton University:* A good case can be made for the chain mechanism. Failure of the nitric oxide test is not positive evidence. The observed acceleration due to nitric oxide may mask an inhibition. This is the case with ethyl ether at higher nitric oxide concentrations.

The Decomposition of Ethyl Bromide and the Collision Theory of First-Order Reactions*

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The reaction $C_2H_5Br \rightarrow C_2H_4+HBr$ has been studied in the neighborhood of 400° with special reference to the effect of the wall surface and the addition of bromine. Earlier experimental facts are summarized and shown to be in agreement with the hypothesis that the primary step is the production of C_2H_5 and Br, followed by chemical reactions which do not involve a long chain. The low pressure effects are explained on the basis of wall effects. The decrease in the value of the first-order rate constant at low pressures can be explained in this reaction and in the decomposition of nitrogen pentoxide without the aid of the collision theory. It is suggested that other examples which have been regarded as confirmations of the collision theory may find similar explanations. It may be necessary to revise the quantitative aspects of the collision theory to allow for a decrease in k at lower pressures than have been heretofore considered.

ETHYL bromide decomposes in the gas phase at about 400° according to a first-order rate equation and gives ethylene and hydrobromic acid with less than five percent of other gases. The chemical analysis of the products and the influence of pressure and foreign gases have been reported earlier.[1-3] In the present work special attention has been paid to the determination of the activation energy and the effect of surface walls, in order to determine more definitely the mechanism by which decomposition occurs and to test the applicability of the collision hypothesis and the hypothesis of free radicals.

Experimental Procedure

The ethyl bromide was prepared from hydrobromic acid and alcohol. The constancy of its freezing point throughout the entire freezing of the liquid showed that the purification was adequate. The decomposition rates checked with those obtained with ethyl bromide prepared by Professor Timmermans in Brussels and distributed by the National Bureau of Standards. Several glass bulbs of about 0.5 cc capacity were filled with the degassed liquid in an all-glass chamber. The removal of dissolved oxygen and other gases was accomplished by successive freezing, evacuation and melting, continuing until no discharge could be obtained with a Tesla coil. The bulbs were sealed and later broken with magnetic hammers when introducing the ethyl bromide into the heated reaction chamber.

The 250-cc spherical flask of Pyrex was provided with a diaphragm and electrical contact for measuring pressures while submerged in a stirred lead thermostat kept constant to 0.1°. A long lever permitted adjustment of the zero point of the diaphragm without removing the vessel from the bath. The all-glass apparatus was cleaned with fuming nitric acid, rinsed and heated while a stream of oxygen passed through to oxidize organic material. Before introducing the ethyl bromide, the whole system was evacuated to 10^{-5} or 10^{-6} cm with a mercury pump while heating.

The special feature of the present technique was a series of capillary gates, the tips of which were broken by rotating a lever in a ground glass joint. The capillary tubes were then sealed off when the entering ethyl bromide had reached the desired pressure. Eight successive experiments could thus be made, each with a new filling, without removing the vessel and without admitting air. In this way it was possible to determine the progressive effect of the products of the reaction on the catalytic behavior of the walls.

Experimental Results

The influence of the walls is seen in Fig. 1 where the pressure increase due to the reaction

$$C_2H_5Br \rightarrow C_2H_4+HBr$$

* Presented at the symposium on "Kinetics of Homogeneous Gas Reactions." See page 725.

[1] E. T. Lessig, J. Phys. Chem. **36**, 2335 (1932).

[2] E. L. Vernon and F. Daniels, J. Am. Chem. Soc. **55**, 922 (1933).

[3] P. Fugassi and F. Daniels, J. Am. Chem. Soc. **60**, 771 (1938).

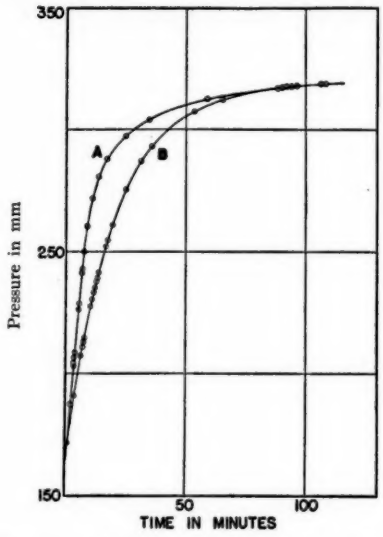

FIG. 1. Decomposition of ethyl bromide at 400°. *A* with cleaned Pyrex walls; *B* with coated Pyrex walls.

is clearly shown for a cleaned flask at *A* and an aged flask at *B*. In the latter experiment the walls were allowed to become coated with the carbonaceous film that is produced by the decomposition of the ethyl bromide.

The specific reaction rate was determined from the slope of the line obtained by plotting log $(2p_i - p_t)$ against time where p_i is the initial pressure of ethyl bromide and p_t is the total pressure of gases at time t. Justification of this formula and the chemical analyses of the products have been given before.[1-3] Hundreds of these graphs have been plotted and in nearly all cases a straight line can be passed satisfactorily through all the points out to about one-third completion. A first-order reaction is thus established. The formula cannot apply throughout the whole course of the reaction because the final pressure is appreciably less than twice the initial pressure, probably on account of the condensation of products on the walls.

Time lag

In the earlier work the evidence regarding the existence of a time lag was not definite. In a few of the experiments the pressure did not seem to rise until after a time longer than that required for the vessel to come to thermal equilibrium. Semenoff[4] commented on this fact and suggested that a chain mechanism may be involved. The experiments described here were designed especially for the study of a possible time lag and the ethyl bromide was introduced in many successive experiments while the flask remained unchanged in the thermostat. Readings could be taken in a fraction of a minute after admitting and sealing off the gas. No time lag was detected at the beginning of the experiments when the initial pressure was more than about 130 mm, but in all twenty-five experiments carried out in the 250-cc vessel below 100 mm there was definite evidence of a time lag. In the most extreme case studied at 400° and an initial pressure of 21 mm, the pressure remained stationary for 15 minutes and then started to rise at a measurable, normal rate. A typical experiment with a time lag is shown in Fig. 2 with pressure-time curves and with the logarithm of concentration plotted against time.

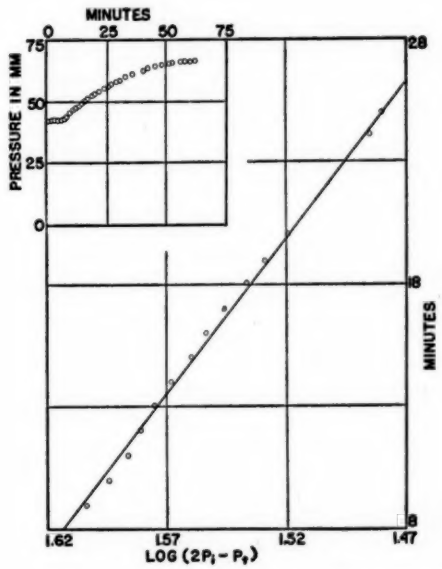

FIG. 2. Decomposition of ethyl bromide at low pressure showing time lag.

Surface effects

In a 250-cc vessel with a surface to volume ratio of 0.9 the specific reaction rate k is two or three times as fast when the surface is freshly cleaned as when it is well coated with the carbonaceous film. In a four-liter vessel it is considerably more than twice as fast. The results of

[4] N. Semenoff, *Chemical Kinetics and Chain Reactions* (Oxford University Press, 1935), p. 450.

a large number of experiments show definitely that although the reaction is catalyzed by a Pyrex surface the activation energy remains constant. However, the measurements made with coated walls are considerably more reproducible, as pointed out by Brearly, Kistiakowsky and Stauffer[5] in experiments on *tert*-butylchloride.

Very serious errors may be introduced in the determination of the activation energy if the surface coating is changed between determinations at different temperatures. This fact is illustrated in a series of eight determinations recorded in Table I and Fig. 3 which were carried out in the 250-cc vessel over a period of several days without removing the flask from the thermostat or admitting air.

The points are plotted on a log k *vs.* $1/T$ graph in Fig. 3 where it is seen that reproducible results are obtained after an aging period of about a day, involving experiments No. 1 and No. 2. Experiments No. 4 and No. 5 give abnormally low values of k because the initial pressures are in the low pressure region. In No. 5 there was an eight-minute time lag and in No. 4 there was a slight lag. The line drawn between experiments 7, 3 and 8, 6 is the most reliable and gives an activation energy of 53,200 which value is substantiated by many other determinations in well-coated flasks. The dotted lines giving activation energies from 20,000 to over 100,000 calories per mole show errors that might have been introduced in determining the activation energy if the measurements at the different temperatures were made while the wall was in the process of being coated. It is quite possible that errors from this changing wall effect may have crept into the measurements of the activation energy of other reactions.

TABLE I. *Effect of changing surface on determination of activation energy.*

EXPERIMENT	AGE	TEMPERATURE	p_i	k
1	New	390°	260 mm	0.00087 sec.$^{-1}$
2	3 hours	380	110	0.00027
3	25	390	146	0.00032
4	29	380	128	0.00017
5	120	390	84	0.00029
6	120	380	182	0.00018
7	144	390	250	0.00034
8	144	380	181	0.00018

[5] D. Brearly, G. B. Kistiakowsky and C. H. Stauffer, J. Am. Chem. Soc. **58**, 43 (1936).

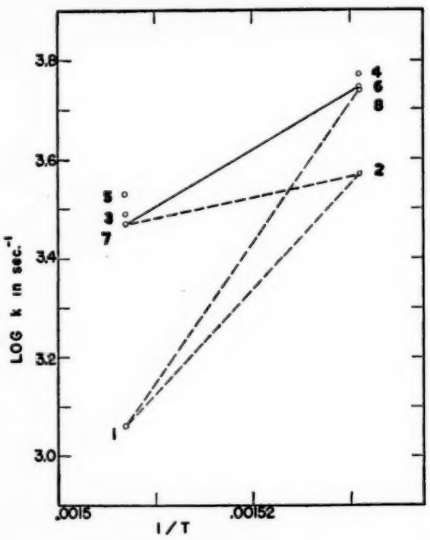

FIG. 3. Calculation of activation energy for ethyl bromide. Full line gives correct value. Broken lines give incorrect values.

The 250-cc vessel having a surface of about 290 cm^2 obtained a normal coating by standing about a day in contact with the decomposition products of the ethyl bromide. After that, the rates were not changed by further aging. In the four-liter vessel (made from two 2-liter flasks) having about 1500 sq. cm of surface the normal, lower values of k were not obtained until after standing thirteen days. The pressure of gas in

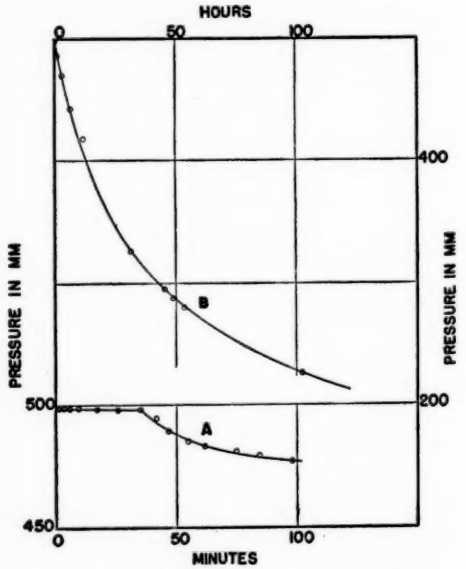

FIG. 4. Decomposition of ethylene at 390°.

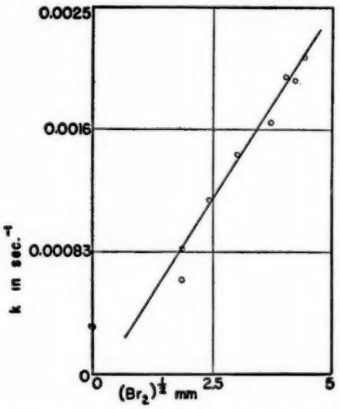

FIG. 5. Influence of bromine on the decomposition.

these experiments was somewhat lower. After the coating had become sufficiently thick the rate constants were the same in the four-liter vessel as in the coated 250-cc vessel.

The time lag is found with both fresh surfaces and coated surfaces. For example in a cleaned flask (250 cc) at 43 mm an initial time lag of six minutes was observed at 390° (Fig. 2) and after the twenty-second consecutive determination in the unopened flask, a time lag of five minutes was obtained at the same temperature with an initial pressure of 65 mm.

It was suspected that this coating on the wall was caused by the polymerization of ethylene which is formed as a product. Accordingly experiments were carried out with purified ethylene using the same vessel and same precautions. One of the resulting pressure-time curves is shown in Fig. 4 where a time lag is definitely shown. After a time lag the pressure starts to decrease and continues for a long time. This reaction has been studied by R. N. Pease.[6]

The film produced on the inside walls of the reaction vessel appeared to be identical with that formed in the ethyl bromide experiments. Moreover, this film produced by the polymerization of ethylene had the same influence on the rate of ethyl bromide decomposition as did the film produced from ethyl bromide itself. It was pointed out in the earlier work that the slow decrease in pressure at the end of an experiment on ethyl bromide is due to the polymerization of the product ethylene. This must account in part at least for the fact that the final observed pressure is always less than twice the initial pressure.

The wall effect was studied further by depositing on the inner walls a heavy silver mirror and then adding bromine after heating and evacuating. A uniform film of silver bromide was produced. The first determination gave a low rate constant (about one-third) probably because the silver had not been completely converted to the bromide. Six more determinations were carried out and a normal rate constant was obtained in every case. Any effect of glass or of silver bromide is apparently destroyed by the carbonaceous film which is deposited.

It is suggested that the deposition of this carbonaceous film on glass surfaces provides a very simple means for destroying the catalytic effect of walls in other gas phase reactions and that the pyrolysis of many organic compounds could well be investigated under these conditions. The film can be easily deposited by heating ethylene above 400° but the oxygen of the air must be excluded because it causes an acceleration of the reactions and after once coming in contact with the film it cannot be easily removed.

Addition of bromine

Bromine is known to accelerate the decomposition of ethyl bromide[1, 3] and its action is important in studying the various reaction mechanisms. Bromine from which oxygen had been boiled out was introduced into a seasoned flask at 390° in amounts up to 18 mm and then ethyl bromide was introduced at 190 mm. The decomposition was accelerated but it still followed the first order with respect to ethyl bromide. The data at 390° in the 250-cc vessel are summarized in Fig. 5 where it is seen that the increase in specific reaction rate is directly proportional to the square root of the bromine concentration, a fact which suggests that bromine atoms are taking part in the reaction. The extrapolation of the line to zero concentration shows that the bromine catalyzes the reaction and suggests that the mechanism may be different.

Two determinations were made at 400° with 12 and 10 mm of bromine giving k values of 0.00188 and 0.00185, respectively. Combining these data with an interpolated value for 11 mm of bromine at 390° an activation energy of 22,000

[6] R. N. Pease, J. Am. Chem. Soc. **51**, 1838 (1929).

calories per mole is obtained. This value is practically half the heat of dissociation of bromine.

It is believed that bromine did not react at these temperatures to give a dibromo ethane. Mixing the products of one of the determinations with a small amount of 3–5 dinitrobenzoic acid, sodium hydroxide and alcohol gave a product ethyl 3–5 dinitrobenzoate, with a sharp melting point at 91°. If the dibromo compound had been present, the melting point would have been lowered. Furthermore, ethylene bromide would not be expected at 390° because it is unstable. Experiments with ethylene chloride gave rate constants of 1.3×10^{-3} and the ethylene bromide would decompose much faster. The earlier experiments[3] with bromine were carried out at 300° where the conditions were quite different.

Addition of nitric oxide

In certain chain reactions, such as the decomposition of the ethers,[7] nitric oxide acts as an inhibitor in small amounts. It is regarded by some as a test for one type of chain reaction. In no case was nitric oxide found to have a retarding effect on the decomposition of ethyl bromide. Even in small quantities the decomposition was accelerated slightly.

Reverse reaction

Several unsuccessful attempts were made to detect a reaction between hydrobromic acid and ethylene. The equilibrium constant has not been determined, but calculations show that the dissociation is nearly complete under the conditions studied. The final pressure of decomposed ethyl bromide is always less than twice the initial pressure and it was suggested[2] that this fact is due to the reverse reaction, but in view of the present experiments the polymerization of ethylene produced in the reaction offers a more satisfactory explanation.

Summary of Observations

The coating of the vessel walls with a carbonaceous film makes possible a greater reproducibility and a more accurate determination of the activation energy. According to the data of the present investigation, the activation energy is 53,200 calories per mole. Taking this value for E, the frequency factor s in the equation $k=se^{-E/RT}$ may be evaluated from the three different researches extending over a period of several years as shown in Table II. It is believed that the last data are the more reliable and accordingly the equation

$$k=1.16\times10^{14}e^{-53,200/RT}$$

is offered as the best value for the decomposition rate of ethyl bromide. It represents the behavior out to at least one-third completion at pressures above 130 mm when the catalytic effect of the walls is repressed and oxygen is excluded. Probably it is valid beyond the one-third completion but the pressure measurements described here are not then applicable. The data of the earlier investigation,[2] in which oxygen was less carefully excluded, were fitted with the equation $k=3.85\times10^{14}e^{-54,800/RT}$.

The experimental facts described here and in the preceding reports may be summarized with the statements of Table III.

Discussion

The primary step cannot be the splitting of the molecule into C_2H_4Br and H because this would require about 90,000 calories per mole and only 53,200 calories is available as determined by the experimental measurements of the decomposition rate at different temperatures.

Table II. *Summary of data for the decomposition rate.*

	Temperature	k observed	s
Vernon	395°C	5.92×10^{-4}	1.53×10^{14}
	405	11.1	1.59
	420	25.0	1.50
Fugassi	395	4.10	1.05
	395	4.20	1.08
Veltman	368.5	0.78	1.04
	379.5	2.05	1.34
	380.5	2.08	1.27
	380.6	2.60	1.13
	388.5	2.93	1.10
	398.5	5.27	1.10
		Average	1.17
	380	1.80	1.14
	380	1.81	1.18
	390	3.40	1.15
		Average	1.16

[7] L. A. K. Staveley and C. N. Hinshelwood, J. Chem. Soc. 1568 (1937).

TABLE III. *Summary of experimental facts.*

1. The reaction $C_2H_5Br \rightarrow C_2H_4+HBr$ proceeds conveniently in the temperature range 370 to 420° and follows the first order to at least one-third completion.
2. The data are fitted by the formula

$$k=1.16\times10^{14}e^{-53,200/RT}$$

at pressures above 130 mm.
3. The decomposition rate is doubled or trebled with clean Pyrex walls and by packing with fresh glass.
4. The catalytic effect of the walls is destroyed by the carbonaceous deposit from the decomposing ethyl bromide or from pure ethylene.
5. In reaction chambers coated with this carbonaceous film, the rate constant k is independent of the size and shape of the vessel.
6. No marked difference in activation energy is observed between the cleaned and coated surfaces, but the accuracy of measurement is not sufficient to distinguish small differences.
7. At pressures below 130 mm the value of the rate constant, k, decreases as the pressure decreases.
8. Below 130 mm there is a time lag at the beginning of the experiment during which the pressure remains constant.
9. The time lag is not observed in the flow experiments when the reaction is followed by the ethylene obtained at the exit.[3]
10. The time lag is roughly the same with coated walls as with clean glass walls.
11. The small amount of gas (5 percent) other than ethylene consists of hydrogen, ethane, propane, butane in decreasing order of abundance.[3]
12. More hydrogen and ethane are obtained with the flow method.
13. Traces of oxygen accelerate the reaction.
14. Bromine accelerates the reaction and the effect is proportional to the square root of the concentration. It does not change the first-order character.
15. Traces of mercury greatly retard the reaction.
16. Nitrogen and hydrogen increase slightly the low pressure value of k and then decrease it.[3]
17. Nitric oxide does not retard the decomposition.
18. Decomposing ethyl bromide causes acetaldehyde to decompose at 350° where the acetaldehyde alone is stable.[8]

The splitting into CH_3 and CH_2Br involves the breaking of the carbon-carbon bond and although there is disagreement concerning this bond energy it is undoubtedly greater than the 53,200 calories which is available. The value is generally taken as 70,000 rendering this step unlikely.

The primary process may be the breakdown into ethyl radicals and bromine atoms. The energy for breaking the carbon-bromine bond is taken as 53,000 although there is some uncertainty involved when, as in this case, a free radical is formed as one of the products. The reverse reaction between free ethyl radicals and a bromine atom can involve very little activation energy so the activation energy for the reaction $C_2H_5Br \rightarrow C_2H_5+Br$ cannot be much larger than 53,000. From energy considerations then, this reaction is quite possible. The unimolecular decomposition directly into C_2H_4 and HBr is also possible. This reaction absorbs 17,800 calories of heat, and the activation energy for the reaction C_2H_4+HBr has been estimated by the semi-empirical method to be about 40,000 calories. The activation energy for $C_2H_5Br \rightarrow C_2H_4+HBr$, then, must be about 58,000 calories and the error of calculation is sufficient for the reaction to go with 53,200 calories.

If the primary step is the formation of C_2H_5 and Br several secondary reactions may result as shown in Table IV.

If the reactions (b) and (c) follow rapidly after (a), making (a) the rate determining step, most all of the facts may be satisfactorily accounted for. This results in a three-step process designated here as mechanism (I). It involves free radicals but it is not a long chain process. The concentrations of C_2H_4Br and C_2H_5 must be very small, but the activation energy E_c is so low that the reaction will still be rapid.

If the decomposition of C_2H_4Br according to Eq. (d) is rapid, the liberated bromine atom will take part in the propogation of a chain by continuing alternations of reactions (b) and (d). This long chain mechanism is designated as mechanism II. Reaction (c) may be regarded as a chain breaking step for mechanism II and the relative importance of I and II is determined simply by the relative rates of reactions (c) and (d).

The straight unimolecular decomposition giving molecules instead of radicals according to reaction (g) is designated as mechanism III.

These three mechanisms and others may now be discussed with reference to the experimental facts listed in Table III.

Undoubtedly the effect of surface walls is important in explaining many of the facts but the wall phenomena are probably of secondary im-

[8] J. Roof and F. Daniels, unpublished.

portance. The striking fact remains that when the polar glass surfaces are covered up with the carbonaceous film and when the initial pressure is kept above 130 mm the decomposition rate is independent of the vessel, the frequency factor is 10^{14} and the reaction behaves as a normal gas phase reaction.

If (a) is slow compared to (b) and (c) (as seems quite likely), and if (c) is fast compared to (d), we can explain the first-order character, the normal frequency factor and the activation energy. If diffusion to the wall is faster than (b) or (d) in the gas phase and if (d) takes place on the wall with the adsorption of ethylene up to a limiting value, we can explain the time lag at low pressures.

The adsorption of free radicals and retention of ethylene or other products on the wall would offset the expected pressure increase and give the observed time lag in the pressure measurements. After the walls become saturated with adsorbed material the normal pressure rise is obtained. Again when the pressure is increased sufficiently, diffusion to the walls is slowed down and reactions (b) and (c) are proportionally more important because reaction (d) cannot compete on the walls. A critical pressure may be expected above which the time lag in the pressure readings would not be observed. In practice such a pressure is noted at about 130 mm.

Mechanism II calls for a long chain reaction. Setting up standard rate equations and steady states it is possible to account for the first-order equation but then the over-all activation energy comes out to be very small. The time lag can be explained on the assumption that it is necessary to accumulate an equilibrium concentration of bromine atoms. The time lag and its restriction to low pressures may be explained also on the hypothesis that reaction (d) occurs on the wall and retains ethylene until the wall is saturated. In mechanism II, however, the over-all activation energy is a function of the several activation energies and there is no reason why it should take on the value 53,000 which seems to be a reasonable value for the primary step, and no reason why the composite frequency factor s should have the normal value of 10^{14}.

Nearly all the experimental facts concerned with the influence of pressure, walls and added foreign gas can be explained by either mechanism I or II. The added bromine accelerates (b) and the effect is proportional to the square root of the bromine concentration. Mercury vapor, on the other hand, reacts with bromine and retards (b). The failure of nitric oxide to inhibit the reaction may possibly be construed as evidence against a long chain by mechanism II.

Mechanism III is sufficient to explain many of the observed facts. The few percent of hydrogen and ethane and propane may be due to a condensation reaction of the product ethylene. The increased rate with fresh glass surfaces may involve adsorption and a slight reduction in the activation energy but the doubling of the decomposition rate demands such a slight change in the activa-

TABLE IV. *Summary of reaction steps.*

I (THREE-STEP REACTION)	
$C_2H_5Br \underset{k'_a}{\overset{k_a}{\rightleftarrows}} C_2H_5+Br$	(a)
$C_2H_5Br+Br \underset{k'_b}{\overset{k_b}{\rightleftarrows}} C_2H_4Br+HBr$	(b)
$C_2H_4Br+C_2H_5 \underset{k'_c}{\overset{k_c}{\rightleftarrows}} C_2H_4+C_2H_5Br$	(c)
II (LONG CHAIN)	
$C_2H_5Br \underset{k'_a}{\overset{k_a}{\rightleftarrows}} C_2H_5+Br$	(a)
$C_2H_5Br+Br \underset{k'_b}{\overset{k_b}{\rightleftarrows}} C_2H_4Br+HBr$	(b)
$C_2H_4Br \underset{k'_d}{\overset{k_d}{\rightleftarrows}} C_2H_4+Br$	(d)
Chain stopping mechanisms	
$2\,Br \underset{k_e}{\overset{k'_e}{\rightleftarrows}} Br_2$	(e)
$C_2H_5Br+Br \underset{k'_b}{\overset{k_b}{\rightleftarrows}} C_2H_4Br+HBr$	(b)
$C_2H_4Br+C_2H_5 \underset{k'_c}{\overset{k_c}{\rightleftarrows}} C_2H_4+C_2H_5Br$	(c)
$C_2H_4Br+Br \underset{k'_f}{\overset{k_f}{\rightleftarrows}} C_2H_4+Br_2$	(f)
$C_2H_5,\ C_2H_4Br,\ Br+wall \xrightarrow{k_g} C_2H_4,\ CH_4,\ H_2,\ HBr,\ C_3H_8,$ etc.	(g)
III (SINGLE STEP)	
$C_2H_5Br \underset{k'_h}{\overset{k_h}{\rightleftarrows}} C_2H_4+HBr$	(h)

tion energy that it cannot be detected with certainty, particularly in view of the lack of consistency obtained with the cleaned glass surfaces. However, the time lag and the marked influence of bromine and traces of oxygen cannot be explained by this mechanism.

The bromine catalyzed reaction can be explained as follows:

$$Br_2 \underset{k_e'}{\overset{k_e}{\rightleftarrows}} 2Br, \qquad \text{(e)}$$

$$C_2H_5Br + Br \underset{k_b'}{\overset{k_b}{\rightleftarrows}} C_2H_4Br + HBr, \qquad \text{(b)}$$

$$C_2H_4Br + Br \underset{k_f'}{\overset{k_f}{\rightleftarrows}} C_2H_4 + Br_2. \qquad \text{(f)}$$

The rate of change of each of the substances C_2H_5Br, Br, C_2H_4Br, Br_2, C_2H_4, HBr and C_2H_5 can be expressed in terms of these equations, giving an over-all equation for the rate of change of pressure dp/dt as follows:

$$\frac{dp}{dt} = k_b\left(\frac{2k_e}{k_e'}c_{Br_2}\right)^{\frac{1}{2}} c_{C_2H_5Br}.$$

Here it is assumed that either k_b' or the concentration of HBr is sufficiently small so that the reverse reaction of (b) may be neglected.

The first-order character of the bromine catalyzed reaction can be explained in this way.

The activation energy for this bromine-catalyzed reaction is low (about 22,000 calories) and one might expect a very rapid reaction. However, the experimental facts of Fig. 5 show that at pressures of a few millimeters of bromine it is only about ten times as fast as the uncatalyzed reaction.

It is thus possible to explain the fact that reaction (a) is still the slow, rate determining step in the uncatalyzed reaction. It is possible to explain also the fact that the free radicals have time to diffuse to the walls at low pressures before reacting.

The Collision Hypothesis

One of the achievements of the collision hypothesis of chemical reactions has been the explanation of first-order gas reactions and the prediction that the specific rate constants will decrease at low pressures.[9–11] The quantitative prediction of the pressure range in which this decrease should occur and the apparent checks with experimental data in several reactions were largely responsible for its ready acceptance.[12–15] Two reactions have been intensively studied in this laboratory for the purpose of checking current theories, and in both cases the data were accepted as supporting the collision hypothesis. The specific decomposition rate of ethyl bromide decreased as the pressure was decreased below 100 mm in agreement with the hypothesis. The fact that nitrogen pentoxide gave a decreasing value of k at pressures below 0.01 mm was regarded as a check even though it was necessary to stretch all the constants to the limit of reasonable values.[16] However, doubt has been expressed[17] that the experimental data of these reactions, and possibly others, necessarily support the quantitative predictions of the collision hypothesis.

In view of the experiments described in the present communication, it seems clear that the decrease in the value of k for ethyl bromide at pressures below 130 mm is due not to the failure of collisions to maintain a steady state of activated molecules as predicted by the collision hypothesis, but that it is due to the fact that the surface effect becomes appreciable when the time required for diffusion to the walls is short. In the case of nitrogen pentoxide, also, recent experiments seem to confirm the prediction[17] that the decrease in k is explainable on the basis of simple chemical reactions. At ordinary pressure nitric oxide, produced by the decomposition of nitrogen pentoxide, reacts with another molecule of nitrogen pentoxide so rapidly that the first step, the unimolecular decomposition, of the nitrogen pentoxide is the rate-determining step. However,

[9] J. A. Christiansen, *Reaktionskinetiske Studies* (Copenhagen, 1921).
[10] F. A. Lindemann, Trans. Faraday Soc. **17**, 599 (1922).
[11] W. H. Rodebush, J. Am. Chem. Soc. **45**, 606 (1923).
[12] C. N. Hinshelwood, Proc. Roy. Soc. London **A113**, 230 (1926).
[13] O. K. Rice and H. C. Ramsperger, J. Am. Chem. Soc. **49**, 1617 (1927).
[14] R. H. Fowler and E. K. Rideal, Proc. Roy. Soc. London **A113**, 570 (1927).
[15] L. S. Kassel, J. Chem. Phys. **32**, 1065 (1928); *The Kinetics of Homogeneous Gas Reactions* (The Chemical Catalog Co., New York, 1932), Chapters V and X.
[16] L. S. Kassel, J. Phys. Chem. **32**, 225 (1928).
[17] F. Daniels, *Chemical Kinetics* (Cornell University Press, 1938), pp. 71, 72.

it has been found recently that the reaction between nitric oxide and nitrogen pentoxide is measurably slow at one mm, and at still lower pressures it may have a rate comparable with that of the nitrogen pentoxide decomposition, thus accounting for the observed decrease in k below 0.01 mm.

In the case of ethyl bromide and nitrogen pentoxide, it is safe to state that the decrease in k observed at lower pressures is not caused by the decreased number of collisions as predicted by the collision hypothesis. It seems likely that a closer examination of other reactions will show that the decrease in k at the lower pressures can be explained in similar ways, by surface effects or competing chemical reactions which become important at low pressures. The experimental facts may not necessarily constitute a unique support of the collision hypothesis.

The fundamental concepts of the collision hypothesis must be correct and at some low pressure the first-order character must change to give a rate which depends on the frequency of collision but it is now suggested that this pressure is lower than heretofore believed.

If this suggestion is correct it will be necessary to re-examine the quantitative aspects of the collision hypothesis. Transfer of energy at molecular collision is probably less efficient than was formerly believed but any revision here would apply to the deactivation rate as well as to the activation rate. The simplest way to account for the maintenance of the first-order rate equation down to still lower pressures is to assume a longer life for the activated molecule. A longer life for the activated molecule may mean simply that it is more difficult to localize in the bond which is about to be broken, the energy which has been accumulated from collisions with other molecules. It is difficult to transfer energy from one mode of vibration to another when the absorbed energy is small and the motion is practically harmonic. It is difficult also when the vibration frequencies are widely different. Possibly the energy of vibrating C—H groups picked up by collision with other molecules cannot easily be transferred to the C—Br vibration.

Possibly this view can be checked with the help of photochemical studies on the rupture of complicated molecules, and on the fluorescence of infra-red radiation.

Discussion

L. S. Kassel: The collisional theory can account for the pressure at which nitrogen pentoxide first deviates from first order, but not so easily for the abruptness of this deviation. The slowness of the reaction

$$NO+N_2O_5 \rightarrow 3NO_2$$

at low pressure should thus be considered a help to the theory rather than a difficulty.

The current interpretation of ethane dehydrogenation as a free radical chain, as presented for example by Rice and Herzfeld at this meeting, seems to require that the primary process is a unimolecular reaction in the second-order region.

The unimolecular character of other reactions, such as the azoalkane decompositions, is certainly at least plausible. The suggestion made by Pease in the last paragraph of his paper, that collisional activation over larger distances may prove necessary, seems uncalled for by present facts. Even the view that no example is known, in which an observed decrease in rate is due to insufficient collisions, causes no difficulty for the present form of the theory. Such difficulty would arise only when some reaction definitely proved unimolecular was found to maintain a first-order rate at a lower pressure than the theory could account for. Such is not the case at present; it seems unnecessary for the theory to be prepared to account for nitrogen pentoxide on the assumption that a slow secondary reaction is quantitatively responsible for the entire decrease in rate down to 0.001 mm, or for other even more hypothetical situations.

Farrington Daniels, *University of Wisconsin:* One can say that the theory is in no need of revision, but I insist that one cannot state that it has been proved in the laboratory.

With reference to the nitrogen pentoxide reaction, we made measurements at 0.01 mm in the

presence of an atmosphere of nitrogen[18] and the specific reaction rate which we obtained falls exactly on the curve through the later low pressure data of Schumacher and Sprenger, Ramsperger and Tolman, and Linhorst and Hodges. In other words, not only does the specific reaction rate start to decrease at such a low pressure that the constants in the collision theory have to be stretched to the limit, but the addition of an inert gas does *not* restore the specific reaction rate to its high pressure value.

O. K. Rice, *University of North Carolina:* I wish to emphasize again my remarks on azomethane made in connection with the previous paper. I believe that it is a good example of a quasi-unimolecular reaction and that it offers considerable quantitative support to the theory.

Something should be said about the work of Koblitz and Schumacher and Schumacher and Frisch on the decomposition of F_2O and F_2O_2. F_2O acts like a quasi-unimolecular reaction which is already in the bimolecular stage; in F_2O_2 the falling-off from the unimolecular rate is quite marked. Both rates are increased in the expected manner by inert gases. The collision rates are just about (as a matter of fact, apparently not quite) sufficient to maintain the reaction if everything is stretched to the limit. Schumacher assumed all classical degrees of freedom, and fairly large radii.

J. A. Christiansen, *Polytechnic Chemical Institute, Copenhagen:* I think that this discussion is not very useful. It seems to be a question of the experimental facts. If a chain reaction is involved one must know exactly what the chain is and how it is stopped.

R. N. Pease, *Princeton University:* I would like to inquire whether anything has been done in coordinating the number of "square terms." Many of us are tired of reading how many equivalent classical square terms are involved. Another thing I hold against the theory is that it has encouraged people to make measurements at very low pressures where much questionable work has been done. It is impossible to carry out chemical analyses but the theory has given certain weight to the pressure measurements.

E. P. Wigner, *Princeton University:* Dr. Kassel has pointed out in his remark that the present theory of quasi-unimolecular reactions cannot predict the pressure at which the unimolecular constant begins to fall off. For some reactions, such as the N_2O_5 dissociation, this occurs at a very low pressure, corresponding to a very large number of active degrees of freedom, for other reactions, such as the N_2O dissociation, at much higher pressures, corresponding to a strongly reduced number of active degrees of freedom. Without questioning the fundamental correctness of the theory, one may well understand the attitude of the experimenters who feel disappointed by the fact that the theory is so flexible that it is not amenable to proof or disproof by experiments. One would be able to make much more definite predictions on the basis of the Rice-Ramsperger-Kassel theory than is possible at present if it were possible to determine the number of active degrees of freedom on the basis of general considerations. This will necessitate a rather close study of the interactions of vibrations etc. in the dissociating molecule.

One can see rather simply that the conditions may be more complicated than we are used to think that they are. As long as we restrict ourselves to a harmonic potential, i.e., neglect the anharmonicity, it is clear that not all molecules which contain the activation energy are really activated. In fact, as long as we neglect anharmonicity, the amplitudes of the different proper vibrations must be in a definite ratio in order to enable the system to reach the activation point. Deviations from this ratio make necessary a larger energy content for the molecule to be dissociated. It follows from this that the number n in the expression $(Q/kT)^{\frac{1}{2}n-1} \exp(-Q/kT)/(\frac{1}{2}n-1)!$ is not equal to the number of square terms in the energy expression but is in general smaller. Its exact value depends on the form of the proper vibrations with respect to the bond to be broken.

Of course, at very low pressures, the molecule will be left alone for a very long time and the anharmonic terms will bring about a redistribution of the total energy among the proper vibra-

[18] J. K. Hunt and F. Daniels, J. Am. Chem. Soc. **47**, 1602 (1925).

tions, until this corresponds to the one in which a dissociation is possible. Under extremely low pressures, therefore, the n in the above expression for the number of activated molecules is equal to the number of square terms in the energy. This corresponds, however, to extremely low pressures.

At higher pressures, only those molecules will be able to dissociate in which the total energy is approximately correctly distributed over the proper vibrations. Thus n will be very much smaller and its value depends on the properties of the proper vibrations. The result of all this is that the zone of transition between bimolecular to unimolecular reaction is very much broader than has been assumed hitherto. Under certain conditions, there may be even an intermediate zone in which the reaction is apparently unimolecular. At any rate, special properties of the dissociating molecule can play a very important role.

O. K. Rice, *University of North Carolina:* In a paper written in 1930 I suggested the possibility of the behavior described by Professor Wigner in his comment. But I do not believe that it is a necessary kind of behavior, and in the case of azomethane which has a reasonable value for n, I do not believe that it occurs.

F. O. Rice, *Catholic University of America:* What is meant by a clean surface? How did you keep the glass walls clean after the first few seconds of the reaction?

Farrington Daniels, *University of Wisconsin:* We cleaned the surface to start with. In successive determinations the specific reaction rate was slower but after three or four experiments, starting with 100 mm of ethyl bromide, the rate constant didn't change any more. Apparently this treatment is sufficient to cover up the active spots on the polar glass surface and give the appearance of a dark film as shown in the photograph. During the first determination or two the progressive increase in the dirtiness of the surface is certainly a complication for the determination of the decomposition rate.

F. O. Rice, *Catholic University of America:* Did you sensitize the reaction?

Farrington Daniels, *University of Wisconsin:* Yes. We mixed ethyl bromide with acetaldehyde at temperatures at which there would be no decomposition of acetaldehyde alone and found that the acetaldehyde decomposed rapidly. We took this as evidence that ethyl bromide in decomposing liberates free ethyl radicals which initiate chains in the acetaldehyde.

I do not believe that there are long chains involved in the decomposition of the ethyl bromide itself.

There is an apparent difficulty. The activation energy for the decomposition of ethyl bromide is 53,800, for methyl bromide it is probably considerably larger, and for propyl bromide it is considerably less (apparently about 36,000 though complicated by isomerization to isopropyl bromide). Each of these decompositions is thought to involve the rupture of the carbon-bromine bond in the primary step, amounting to about 53,000 calories.

R. A. Ogg, Jr., *Stanford University:* The difference in activation energy must be due to a difference in the behavior of the radicals and the rapid subsequent reactions which the heavier radicals can undergo.

Farrington Daniels, *University of Wisconsin:* For those interested in settling the controversy regarding the pressure effect on unimolecular reactions, there are at least two lines to follow. The theorists should try to make calculations regarding the movement of energy inside of complex molecules and the experimentalists must certainly get more reliable data on simple gas reactions at very low pressures. Pressure measurements which include the gross effect of several reactions and possible wall effects are not very satisfactory. New techniques and new methods of following reactions by optical or other physical or chemical methods are needed. Large scale experiments with very large tubes to minimize wall effects would be valuable.

Fluorescence and Photochemical Kinetics of Polyatomic Molecules in the Gas Phase *

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Various mechanisms for the excitation and quenching of fluorescence are discussed. It is pointed out that the classical Stern-Volmer mechanism may apparently be obeyed in cases where the process is not that of simple absorption followed by fluorescence and collisional deactivation. For polyatomic molecules a spectroscopic examination will not always disclose definitely the nature of the emitting radical or molecule. A study of the effects of several variables on the intensity of the fluorescence will frequently give much information about the lifetimes of the emitting molecules and the course of the photochemical reactions taking place. Quantitative studies of the fluorescence in the gas phase have been made for very few polyatomic molecules. Nitrogen dioxide and acetone are cited as examples.

IN THE simple case in which molecules of a gas absorb monochromatic radiation, excited molecules in one energy level are formed if the absorption spectrum is truly discrete. These excited molecules may either be deactivated by collision with other molecules or fluoresce. These three processes give rise to a Stern-Volmer mechanism[1] which may be represented as follows:

$$A+h\nu=A', \tag{1}$$

$$A'+A=A+A, \tag{2}$$

$$A'+M=A+M, \tag{3}$$

$$A'=A+h\nu'. \tag{4}$$

Primed letters refer to excited molecules and unprimed letters to molecules which, at least, are incapable of emitting fluorescent radiation. Let I_a be the number of quanta absorbed per cubic centimeter per second and I_f the number of quanta emitted as fluorescence per cubic centimeter per second and also let all concentrations be expressed in molecules per cubic centimeter. The assumption of a steady state for excited molecules in the volume element dv leads to the following equation:

$$1/Q=I_a/I_f=1+\frac{k_2(A)+k_3(M)}{k_4}, \tag{5}$$

where the subscripts for the k's correspond to the equations for which they are the specific reaction rates. In the derivation of Eq. (5) we have assumed either that the excited molecules have such short lives that they cannot diffuse out of the volume element dv or that the rate of diffusion of excited molecules into the volume element is equal to the rate of diffusion out. If these assumptions are not valid, as might be the case with long-lived excited molecules or with a high absorption coefficient of the absorbing gas, corrections are necessary.

In any actual apparatus the fluorescence emitted from a finite volume will be observed. Moreover, the entire radiation from this volume will not be incident upon the measuring instrument. If a parallel beam of radiation is employed and the fluorescence is observed from a volume of length l and cross section A, the number of quanta absorbed per second will be

$$I_0(1-\exp(-k(A)l))A, \tag{6}$$

where I_0 is the number of quanta per second incident on the volume per square centimeter.

If the fraction of the fluorescent radiation intercepted by the measuring apparatus varies from one part of the volume to another, spurious results may be obtained as the pressure is varied unless the absorption coefficient is so low that the number of quanta absorbed per cubic centimeter per second is almost independent of l.

The rate of formation of excited molecules per unit volume now becomes

$$I_0(1-\exp(-k(A)l))A/v, \tag{7}$$

where v is the volume from which fluorescence is observed. If a is the fraction of the quanta fluoresced in the volume which is intercepted by the measuring instrument and if b is the factor

* Presented at the symposium on "Kinetics of Homogeneous Gas Reactions." See page 725.

[1] O. Stern and M. Volmer, Physik. Zeits. **80**, 183 (1919).

which converts the number of quanta per second incident on the measuring apparatus into arbitrary units (cm deflection, etc.), the rate of emission of fluorescent quanta per unit volume becomes

$$D_f/vab, \tag{8}$$

where D_f is the deflection observed.

Again assuming a steady state for excited molecules we obtain

$$I_0(1-\exp(-k(A)l))A = \left(1+\frac{k_2(A)+k_3(M)}{k_4}\right)D_f/ab. \tag{9}$$

If (A) is maintained constant, a plot of I_0/D_f against (M) will give a straight line. The slope of this line will be

$$\frac{k_3}{k_4abA(1-\exp(-k(A)l))} \tag{10}$$

and the intercept with the axis will be

$$\frac{(1+k_2(A)/k_4)}{abA(1-\exp(-k(A)l))}. \tag{11}$$

Dividing the slope by the intercept cancels several of the arbitrary (or difficultly determinable) constants and gives

$$\text{Slope/intercept} = k_3/(k_4+k_2(A)) = W. \tag{12}$$

If a study is made in which $(M)=0$ and (A) is varied, a plot of $(I_0/D_f)(1-\exp(-k(A)l))$ against (A) should give a straight line and

$$\text{Slope/intercept} = k_2/k_4 = X. \tag{13}$$

From X and W it is possible to calculate k_2/k_4, k_3/k_4, and k_2/k_3. It is impossible to evaluate any of these constants individually unless both the absorbed and fluorescent intensities can be determined in absolute units at very low pressures.

k_2 and k_3 may be written in the form

$$2f\sigma^2(2\pi kT/M)^{\frac{1}{2}}\exp(-\Delta E/RT), \tag{14}$$

where M is the reduced mass, k is the Boltzmann constant, T is the absolute temperature, and σ is the sum of the radii of the excited and quenching molecules. f is an efficiency factor, but since f and σ may not be determined independently, it is customary to place $f=1$. σ_2^2 and σ_3^2 would be termed effective cross sections for quenching and would, in general, not be identical with values obtained from viscosity measurements on gases. The energy of activation, ΔE, for the quenching process has usually been assumed to be small or zero.

Since the quenching of fluorescence must necessarily involve the transition of a molecule from an upper to a lower energy surface, Eyring's treatment of nonadiabatic reactions is certainly applicable to this process.[2] Fig. 1 is a schematic representation of the energy surfaces. Curve I is the potential surface for the interaction of an excited and a normal (quenching) molecule and curve II that for two normal molecules. ϵ_{12} is the minimum energy difference between the two surfaces at their point of nearest approach, and S_1 and S_2 are the slopes of the surfaces at these points. ΔE is the energy of activation for the process.

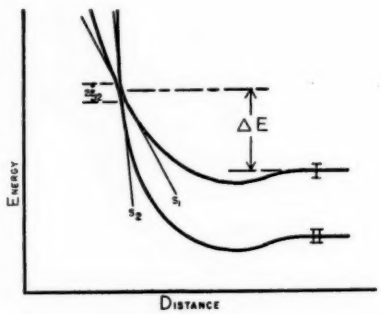

FIG. 1.

The specific reaction rate for quenching may now be written in the form

$$k_q = \kappa(kT/h)\exp(\Delta S/R)\exp(-\Delta E/RT), \tag{15}$$

where κ is the transmission coefficient. In this case

$$\kappa = 2p(1-p), \tag{16}$$

where[3]

$$p = \exp(-4\pi^2\epsilon_{12}^2/hV|S_1-S_2|). \tag{17}$$

V is the velocity of the point representing the system on surface I near the intersection.

Two cases may be considered:

[2] M. G. Evans, H. Eyring and J. F. Kincaid, J. Chem. Phys. **6**, 349 (1938).

[3] C. Zener, Proc. Roy. Soc. **A137**, 696 (1932); **A140**, 660 (1933). L. Landau, Physik. Zeits. Sowjetunion **2**, 46 (1932).

Case I

If ΔE is large, p approaches zero, and Eq. (15) reduces to

$$k_q = 2p(kT/h)(\exp(\Delta S/R))\exp(-\Delta E/RT) \quad (18)$$

or
$$d \ln k_q/dT \cong \Delta E/RT^2. \quad (19)$$

There would be therefore a large temperature coefficient for quenching.

Case II

If ΔE is small, we obtain

$$k_q = 2p(1-p)(kT/h)\exp(\Delta S/R) \quad (20)$$

and the temperature coefficient of the rate of quenching will be very small and, moreover, will be positive or negative depending upon $\partial\Delta S/\partial T$.

Returning now to the mechanism embodied in Eqs. (1–4) several difficulties in interpretation of data may be cited.

(1) If several lower levels exist to which A' may go with emission of radiation, k_4 must be replaced by a summation of constants, one for each possible transition. Thus the Stern-Volmer mechanism will apparently be obeyed, but quenching experiments will give only the sum of the decay constants.

(2) If quenching may occur to more than one nonradiating energy level, either k_2 or k_3 or both must be replaced by summations. Once again the Stern-Volmer mechanism will apparently be obeyed, but no information can be obtained from quenching concerning the relative amounts of the various types of quenching. Thus the $6\,^3P_1$ state of mercury may be quenched either to the $6\,^3P_0$ or to the $6\,^1S_0$ state but the sum of the quenching constants would be obtained from fluorescence experiments.

(3) In the particular case in which $\nu = \nu'$, the fluorescent radiation will be absorbed by the A molecules thus leading to *radiation imprisonment*. This effect is troublesome in experiments with mercury vapor where the absorption coefficient of the 2537A line is high and can be dealt with theoretically only in apparatus of simple geometrical form.[4, 5] Generally, imprisonment leads to a low *apparent* value for k_4 and renders conclusions about effectiveness of quenching invalid.[6]

(4) If the absorbed radiation may not be treated as strictly monochromatic, conclusions will usually be invalid if the absorption coefficient for any part of the radiation is very high. Expression (6) must then be replaced by a double integral over all frequencies and over the distance.[7] This particular difficulty is not of great importance in dealing with most polyatomic molecules but influences very greatly the results on mercury where Beer's law is valid only for a differential range of frequencies.

(5) The form of the absorption line may change with the pressure of either A or M. Thus a redistribution of absorption in the illuminated zone may take place as the pressure is varied. This may not be serious although it would usually result in a lack of constancy for a introduced above. Since b also will be open to suspicion, a careful consideration should be given to this matter before attempting a theoretical interpretation of experimental results.

(6) If A' may undergo any other first-order reaction than (4) (for example, if it has a finite probability of predissociating), Eq. (5) becomes

$$1/Q = 1 + k_4'/k_4 + (k_2(A) + k_3(M))/k_4, \quad (21)$$

where k_4' is the sum of the specific reaction rates for all other first-order processes than fluorescence. Eq. (9) will be modified in a similar way. Thus slope divided by intercept will be

$$k_3/(k_4 + k_4' + k_2(A)) \quad (22)$$

instead of (12). Quenching experiments cannot lead to individual values of k_4 and k_4' even if k_3 is known. However $1/(k_4 + k_4')$ will still be the mean life of molecules in the excited state in the absence of collision.

With simple monatomic vapors usually only one upper state and one frequency of fluorescent emission need to be considered. With di- and polyatomic molecules this is not the case. If the incident radiation is strictly monochromatic, only one excited energy level will be produced by the absorption act. However, from this level there will exist transitions to a variety of vibra-

[4] A. A. Milne, J. Lond. Math. Soc. **1**, 1 (1926).
[5] M. W. Zemansky, Phys. Rev. **36**, 919 (1930).
[6] H. W. Melville, Proc. Roy. Soc. **A152**, 325 (1935).
[7] W. A. Noyes, Jr., Cold Spring Harbor Symposium on Quant. Biology, **3**, 32 (1935).

tion (and rotation) levels of the ground state, the distribution of intensity in the fluorescent radiation being governed by selection rules and by the Franck-Condon principle. These facts alone would not invalidate the form of the Stern-Volmer equation as pointed out above.

Collisions may also produce a redistribution of molecules in various rotation and vibration energy levels each with its own transition probability for fluorescence. The radiation will now be polychromatic to a degree depending, perhaps, on the collision frequency. The characteristics of the measuring device will affect very markedly the results obtained. In order to obtain values which have theoretical significance, the measuring device should determine a quantity proportional to the number of quanta of fluorescent radiation emitted regardless of frequency. Almost no light-sensitive apparatus fulfills these requirements rigorously although some photographic plates and a few photoelectric cells may suffice over a limited range of wave-lengths. Thermopiles would be particularly bad since the response is proportional to the incident energy and not to the number of quanta.

The equation for $1/Q$ in the event that collisions cause a redistribution among energy levels has been worked out for several cases and applied. The mechanism may be represented as follows:

$$A+h\nu=A^0, \tag{23}$$

$$A^i+A=A^i+A \qquad (i=0, 1, \cdots n), \quad (j=0, 1, \cdots n), \tag{24}$$

$$A^j=A+h\nu^j \qquad (j=0, 1, \cdots n), \tag{25}$$

$$A^j+A=A+A \qquad (j=0, 1, \cdots n), \tag{26}$$

$$A^j=\text{products} \qquad (j=0, 1, \cdots n). \tag{27}$$

The resulting equation is

$$1/Q=1+(\sum_0^n(k_{26}{}^j(A)+k_{27}{}^j)\Pi_j{}^n)/\sum_0^n k_{25}{}^j\Pi_j{}^n. \tag{28}$$

$\Pi_j{}^n$ is an nth degree polynomial in (A).

At low pressures Eq. (28) reduces to

$$1/Q=1+(k_{26}{}^0(A)+k_{27}{}^0)/k_{25}{}^0 \tag{29}$$

and at high pressures one obtains an equation of the form

$$1/Q=\alpha+\beta(A). \tag{30}$$

Since (28) is an $(n+1)$th degree polynomial in (A), the number of roots may be as large as the number of states which fluoresce. Both at very low and at very high concentrations of A, straight lines of the Stern-Volmer type will be observed. From the slope/intercept ratio for the low pressure part of the graph the constants for the state A^0 could be evaluated. If the quenching is by simple monatomic or diatomic molecules, only small changes in vibration quantum number will be expected, and the constants k_{25} will not differ greatly. With complex molecules many more vibration levels of the upper state may be involved.

Equation (28) contains so many arbitrary constants that it could be made to fit almost any data providing the fluorescent radiation from the initially formed state affects the measuring instrument.

An analogous case for quenching of iodine fluorescence by foreign gases has been worked out.[8] In this case, as shown by Rabinowitch and Wood,[9] quenching results from a dissociation of the excited molecules, but that fact will not alter the form of the equation.

The mechanisms given in the preceding paragraphs should account for all of the cases in which the absorbing molecules emit fluorescent radiation. Very often fluorescence due to the dissociation products is found, and particularly with polyatomic molecules, the nature of the primary processes may be inferred from the spectrum of the fluorescence. Thus nitric oxide bands are emitted when nitrous oxide is irradiated in the Schumann region,[10] hydroxyl bands are emitted by H_2O, CH_3OH, HCOOH, and CH_3COOH[11], and cyanogen bands are emitted by CH_3CN[11]. NH_3 and CH_3NH_2 emit bands which have been ascribed to NH_2 free radicals.[11]

If one of the products emits radiation, imprisonment will usually be unimportant.

We may now examine several mechanisms which lead to a Stern-Volmer form of equation.

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[8] J. F. Koehler, Phys. Rev. **44**, 761 (1933); J. P. Howe and W. A. Noyes, Jr., J. Am. Chem. Soc. **57**, 1262 (1935).

[9] E. Rabinowitch and W. C. Wood, J. Chem. Phys. **4**, 358 (1936).

[10] P. H. Sen-Gupta, Proc. Roy. Soc. **A146**, 824 (1934).

[11] A. Terenin and H. Neujmin, J. Chem. Phys. **3**, 436 (1935).

1. $$AB_2+ h\nu = A+ B_2', \quad (31)$$

$$B_2' = B_2+ h\nu', \quad (32)$$

$$B_2'+AB_2 = B_2+AB_2. \quad (33)$$

The fate of A is immaterial as long as it does not react in such a way as to affect the fluorescence. By the usual assumptions one finds

$$1/Q = 1+k_{33}(AB_2)/k_{32} \quad (34)$$

and the ratio of slope to intercept will give the same information concerning B_2' as was obtained previously for the optically excited molecules. If B_2' may fluoresce to several energy levels, k_{32} will be replaced by a summation, and if collisions lead to a redistribution among energy levels each with its own specific rate of decay, an equation of the type of (28) will be obeyed.

No quantitative studies of fluorescent intensity seem to have been made for molecules which follow this mechanism. Such cases must exist particularly with salt vapors and with the molecules just cited.

2. $$AB_2+h\nu = AB+B, \quad (35)$$

$$AB+AB = (AB)_2', \quad (36)$$

$$(AB)_2'+AB_2 = (AB)_2+AB_2, \quad (37)$$

$$(AB)_2' = (AB)_2+h\nu', \quad (38)$$

$$1/Q = 2(1+k_{37}(AB_2)/k_{38}). \quad (39)$$

This case is probably more simple than would be found in actual practice but may be approached in certain instances. Eq. (36) postulates that two atoms or radicals in their normal states may come together to form an excited molecule. The existence of this molecule would have to be sufficiently long to permit it to fluoresce. With diatomic molecules this would be very improbable. Since the "time" of a collision is of the order of magnitude of 10^{-13} second and lifetimes in excited states are of the order of 10^{-7} second, the probability of emission would be about 10^{-6}. With polyatomic molecules of many degrees of freedom the inverse of the process postulated by Rice and Ramsperger[12] and by Kassel[13] for unimolecular reactions would be important, and emission of radiation from the excited state would be much more probable.

That two states which may combine with each other optically can be formed from atoms in their normal states is known for diatomic molecules (*viz.*, the $X^1\Sigma_g^+$ and $A1_u$ states of I_2 for which a weak transition is observed in absorption and the $X^3\Sigma_g^-$, $A^1\Sigma_g^+$, and $C^3\Sigma_u^+$ states of O_2).

Other cases might be cited which would follow a Stern-Volmer equation, but it is evident from the few examples given that agreement with that equation does not signify that the excited molecules formed during absorption emit fluorescent radiation.

We may turn our attention to a few other types of mechanism which might be of interest to photochemists.

1. $$AB_2+h\nu = AB+B, \quad (40)$$

$$AB+AB = (AB)_2', \quad (41)$$

$$(AB)_2' = (AB)_2+h\nu', \quad (42)$$

$$(AB)_2'+AB_2 = (AB)_2+AB_2, \quad (43)$$

$$(AB)_2' = 2AB, \quad (44)$$

$$AB+AB = (AB)_2'', \quad (45)$$

$$(AB)_2'' = 2AB, \quad (46)$$

$$(AB)_2''+AB_2 = (AB)_2+AB_2. \quad (47)$$

This is an extension of the mechanism embodied in Eqs. (35–39). The prime refers to an excited state which may fluoresce, and the double prime refers to a high vibration level of the ground state which may either redissociate or be deactivated by collision. It is not worth while to give the detailed expression for $1/Q$, but it turns out to be a quadratic in (AB_2).

The relative probabilities of forming $(AB)_2'$ and $(AB)_2''$ by collision is a matter of some interest. An extension of the method of Zener and Landau[3] might be used. The ratio of the probabilities should be of the order of magnitude of unity.

2. By introducing other fluorescing states into the mechanism (40–47), $1/Q$ will be in the form of an $(n+1)$th degree polynomial where n is the number of fluorescing states.

3. If the free radical AB can dissociate into A and B, the expression becomes exceedingly com-

[12] O. K. Rice and H. C. Ramsperger, J. Am. Chem. Soc. **49**, 1617 (1927).
[13] L. S. Kassel, J. Phys. Chem. **32**, 225 (1928).

plicated and involves terms in the square root of the reciprocal of the light intensity.

When we turn our attention to the application of these ideas to actual cases, we find a dearth of quantitative experimental work. Fluorescence has been observed qualitatively in many gases, and for a few the spectra have been photographed. Thus information is available as to the nature of the fluorescent emitters.

If fluorescence is observed at moderate pressures (several hundred millimeters), the excited states must be relatively insensitive to collisions. With polyatomic molecules fluorescence seems to be observed at such pressures only if more than one resonance structure can be written. Common examples are nitrogen dioxide, biacetyl, benzene and certain unsaturated hydrocarbons.

The two polyatomic gases for which quantitative data of any description seem to be available are nitrogen dioxide and acetone (or biacetyl).

Nitrogen dioxide shows absorption at room temperature from about 6000A toward shorter wave-lengths. At approximately 3700A the bands become visibly diffuse. Photochemical decomposition with a low yield is observed at 4050A although none is found at 4360A.[14]

Baxter[15] has investigated the fluorescence over a wide range of pressures using radiation containing both the 4050A and 4360A lines of mercury. Over the pressure range used (0.00117 mm to 18.3 mm) a Stern-Volmer mechanism was found to be obeyed although due to the use of a visual method for intensity measurements, the scattering of the points was quite large especially at low pressures.

The maximum absorption coefficient for nitrogen dioxide lies in the neighborhood of 4000A.[16] This means that in the studies of Baxter the transition coefficient from low vibration levels of the ground state to the upper state is a maximum. Nevertheless only two fluorescence bands were observed with wave-lengths 5900A and 6400A. While the wave-length of the incident radiation was not varied, other cases show no change of emitted light with incident frequency at moderate pressures. This may best be interpreted by assuming that molecules in the upper state lose all or nearly all of their vibrational energy before they fluoresce. The frequency difference between the two bands (1330 cm^{-1}) will be a ground state difference and may be compared with the symmetrical frequency 1370 cm^{-1} observed in the infra-red spectrum of nitrogen dioxide.[17] Thus the most probable transition from the 0th vibration level of the upper state is to $v''=3$ or 4.

At first glance, therefore, the mechanism embodied in Eqs. (23)–(27) should apply to nitrogen dioxide. At very low pressures (just how low is difficult to determine) the upper state (or states) formed by optical absorption must fluoresce. At higher pressures, including most of the range investigated by Baxter,[15] the chance of loss of vibrational energy before fluorescence is very great. Thus a Stern-Volmer equation cannot be obeyed at all pressures. The data of Baxter scatter too much at low pressures to make any conclusions possible.

If the scheme embodied in Eqs. (23)–(27) is obeyed, a plot of $1/Q$ *vs.* (A) cannot give a straight line over the entire pressure range. Nevertheless, from the ratio of slope to intercept at high pressures certain conclusions can be drawn, particularly if loss of vibrational energy by the excited molecules due to collisions is so much more probable than a gain that the latter may be neglected. Dissociation will also be negligible if the 4360A line is the main one absorbed,[16] and loss of one quantum of vibration at a time will be much more probable than larger losses.

Equation (30) will be of the proper form to represent $1/Q$ at *high* pressures, and with the assumptions made in the preceding paragraph, it may be shown that

$$\alpha/\beta=\sum_{0}^{n}\frac{k_{25^j}+k_{27^j}}{k_{24^{j,\,j+1}}+k_{26^j}} \quad \text{where} \quad k_{24^{n,\,n+1}}=0, \tag{48}$$

$$1/\tau=2K(\alpha/\beta)/(n+2), \tag{49}$$

where n is the number of upper states in addition to the state formed by optical absorption, and K is given by (14) providing σ, f, and ΔE are the same for all of the collision processes considered. τ is the average mean life of all the excited states.

If these simplifying assumptions are not valid,

[14] R. G. Dickinson and W. P. Baxter, J. Am. Chem. Soc. **50**, 774 (1928).
[15] W. P. Baxter, J. Am. Chem. Soc. **52**, 3920 (1930).
[16] H. H. Holmes and F. Daniels, J. Am. Chem. Soc. **56**, 630 (1934).
[17] H. Sponer, *Molekülspektren* (Julius Springer, Berlin, 1935), Vol. I, p. 78.

little or no meaning can be attached to mean lives and collision diameters obtained from the ratio of slope to intercept for data obtained at high pressures.

The collision diameters and mean lives found by Baxter[15] have, therefore, only a rough statistical meaning. It would be interesting to carry out more precise measurements at low pressures where the constants for the initially excited state might be obtained.

The fluorescence of acetone is an interesting case about which to speculate. This fluorescence was observed by Damon and Daniels[18] who found it to be excited by all wave-lengths between 3130A and 2537A. Norrish, Crone and Saltmarsh[19] found no fluorescence to be excited by the shorter wave-lengths of this region.

A Stern-Volmer equation was found to be obeyed at relatively low intensities and moderate pressures (over 50 mm).[20] Later work[21] showed that with high incident intensities the intensity of the fluorescence increased with time leading to the conclusion that one of the products of the reaction was involved. A spectroscopic investigation showed the fluorescent bands to be the same for biacetyl as for acetone. Almy, Fuller, and Kinzer[22] have confirmed this result and have shown that the fluorescence of acetone excited by 3130A is identical with that of biacetyl whether the latter is excited by 3130, 3650, 4047, or 4358A.

Whether any fluorescence of acetone takes place is uncertain. Perhaps the weak blue fluorescence observed by Damon and Daniels[18] is to be ascribed to acetone, but the bands 5117, 5572, and 6095A reported by various authors[19, 23] are almost certainly due to biacetyl.

Since the fluorescent bands are independent of exciting wave-length, the same distribution among upper state vibration levels seems to exist at the pressures used regardless of the energy of the quanta absorbed. The frequency differences between fluorescence bands are, therefore, characteristic of the ground state of biacetyl. These differences are, approximately, 1540 and 1596 cm^{-1}. If second differences are constant, as would be the case if only one anharmonic term need be considered, $v''=2$, 3, and 4 providing high values of the $>C=0$ frequency (1725 cm^{-1})[24] are involved.

Since the spectrum of biacetyl is emitted under conditions such that the partial pressure of this substance is exceedingly small, direct optical excitation of this molecule may be ruled out. We have, therefore, two possibilities: (*a*) the biacetyl spectrum is excited by collisions of the second kind with excited acetone molecules; and (*b*) some mechanism similar to one of those outlined above involving the combination of free radicals is obeyed. Enough energy is not absorbed by the acetone to cause dissociation with resultant excitation of either free radical to fluorescence unless the energy required to dissociate the carbon-carbon bond is lower than is usually supposed. Considerations based on conservation of energy and of momentum make excitation by collision of the second kind relatively improbable when the molecules possess so many degrees of freedom. This possibility cannot, however, be excluded with certainty.

Since at least two resonating structures may be written for biacetyl, two acetyl radicals may come together to form either a normal or an excited molecule. The carbon-oxygen distances would be different in upper and lower states, and the carbonyl frequency would probably be found in the emission bands.

Either the mechanism (35)–(39) or the mechanism (40)–(47) might apply although collisions causing distribution among energy levels would have to be introduced in view of the results of Almy, Fuller, and Kinzer.[22] The mechanism (35)–(39) gives a straight line at all pressures while (40)–(47) will give a straight line at sufficiently high pressures.

The effect of biacetyl in causing an increase in fluorescence must still be explained. This may be accomplished if one introduces a reaction suggested by Taylor and Jungers[25] to explain the low quantum yield of acetone decomposition

[18] G. H. Damon and F. Daniels, J. Am. Chem. Soc. **55**, 2363 (1933).
[19] R. G. W. Norrish, H. G. Crone and O. D. Saltmarsh, J. Chem. Soc. 1456 (1934).
[20] C. F. Fisk and W. A. Noyes, Jr., J. Chem. Phys. **2**, 654 (1934).
[21] M. S. Matheson and W. A. Noyes, Jr., J. Am. Chem. Soc. **60**, 1857 (1938).
[22] G. M. Almy, H. Q. Fuller and G. D. Kinzer, Phys. Rev. **55**, 238 (1938).
[23] R. Padmanabhan, Proc. Ind. Acad. Sci. **5A**, 594 (1937).
[24] K. W. F. Kohlrausch and A. Pongratz, Ber. **67B**, 976 (1934).
[25] H. S. Taylor and J. C. Jungers, Trans. Faraday Soc. **33**, 1353 (1937).

$CH_3+(CH_3CO)_2=CH_3COCH_3+CH_3CO.$ (50)

Spence and Wild[26] find a ratio of carbon monoxide to ethane from photochemical acetone decomposition of 1 : 1 at 3130A. In view of the nature of the fluorescence a strict adherence to this ratio would seem to be impossible, and a further study of this matter should be made. The mechanism suggested above for the fluorescence is definitely wrong unless fluorescence is observed at all wave-lengths at which biacetyl is formed. Since fluorescence was observed[18] at all wave-lengths from 3130A to 2537A, biacetyl must be formed throughout this range of wave-lengths. However, the following supposed facts would, if true, render the interpretation doubtful: (*a*) The intensity of the fluorescence is a maximum at about 2800A;[19] (*b*) no fluorescence is observed when acetone is irradiated by wave-lengths between 1800 and 2000A even though the quantum yield of carbon monoxide formation is not unity;[27] and (*c*) fluorescence is observed at temperatures over 100°C where biacetyl formation takes place to a small extent if at all. The objections here raised are surmountable.

Support is found for the mechanism suggested from the fact that ethyl methyl ketone, which also gives diketones on irradiation,[28] shows the same structure of fluorescence bands as acetone.[23] Other compounds which might give biacetyl upon irradiation would be worth investigating as would the fluorescences of such molecules as formaldehyde, glyoxal, and methyl glyoxal.

[26] R. Spence and W. Wild, J. Chem. Soc. 352 (1937).

[27] J. P. Howe and W. A. Noyes, Jr., J. Am. Chem. Soc. **58**, 1404 (1936).

[28] V. R. Ells and W. A. Noyes, Jr., J. Am. Chem. Soc. **60**, 1864 (1938).

Discussion

R. A. Ogg, Jr., *Stanford University:* What is the particular significance of the resonating structure of biacetyl?

W. A. Noyes, Jr., *University of Rochester:* If there are two resonating structures there can be two or more states of a molecule formed from component radicals in normal states. The acetyl radicals have the opportunity of forming excited biacetyl which will give off radiation on going to the ground state.

D. C. Grahame, *University of California:* Another piece of experimental evidence in connection with this point is the observation that acetaldehyde doesn't fluoresce with light of wave-lengths below 2800A, or at most only very slightly. If free radicals are formed with radiation below 2800A there should be recombination of acetyl radicals here also, and one would then expect to observe fluorescence.

W. A. Noyes, Jr., *University of Rochester:* The addition of biacetyl to acetone increases the intensity of fluorescence. Since biacetyl is formed there must be acetyl radicals present in the reaction.

P. A. Leighton, *Stanford University:* Have you been able from your streaming experiments to determine the rate of decay of the luminescence? The rate of decay should provide one of the strongest indications as to whether it is a true fluorescence or a chemiluminescence arising from the combination of radicals.

J. G. Winans, *University of Wisconsin:* The re-emitted fluorescent line would be difficult to observe because it might be largely absorbed whereas the chemiluminescent line would not.

W. A. Noyes, Jr., *University of Rochester:* That would be true if the absorption coefficient were high. In this case we are dealing with only 10 to 20 percent absorption and I don't believe that all the fluorescent light could be absorbed.

J. G. Winans, *University of Wisconsin:* It might be possible to account for the large wave-length difference between the absorbed and emitted wave-lengths observed for NO_2 by emission to an excited electronic state instead of redistribution among the vibrational levels as suggested. The two cases could be distinguished by observing the wave-lengths of the fluorescence light at different pressures. If the wave-length changed with pressure, the redistribution among vibrational levels would be indicated, while if there was no change in wave-length with pressure, the emission to an excited electronic state would be most likely.

The Effect of Temperature on the Predissociation of Photoactivated Acetaldehyde Molecules*

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The relative efficiencies of production of free radicals in acetaldehyde by the absorption of light of the wave-lengths 3132 and 2652A have been studied by observing the quantum yields of the photochemical reaction at high temperatures. It has been found that at room temperature more radicals are produced by the absorption of $\lambda=2652$A than by $\lambda=3132$A. As the temperature is raised, the yield of radicals at the longer wave-length increases relative to that at 2652 until at 100°C the two are equal. At higher temperatures the longer wave-length has the greater efficiency for the production of radicals. This change with temperature is accounted for by assuming that at $\lambda=3132$A the dissociation is aided by thermally excited vibrational energy. In accordance with this assumption it is found that as the temperature is raised the fluorescence, which is easily visible at room temperature, fades in a manner which is roughly parallel to the increase in dissociation. There is no evidence for such a thermally induced predissociation with $\lambda=2652$A. The lower efficiency of production of free radicals at $\lambda=2652$A is believed to be due to a difference in the electronic states reached by acetaldehyde excited by the two wave-lengths.

THE importance of the role of free radicals in the photolysis of acetaldehyde has been a subject of discussion for some time. There can be no doubt that free radicals are formed under some conditions since they have been detected by means of the reaction with lead mirrors.[1] At the longer wave-lengths, especially those greater than the limit of the predissociation blurring in the spectrum, it may be said that the light quantum has insufficient energy to cause the dissociation.[2] However, it is possible that even under these conditions the molecules may dissociate after photoactivation with the aid of energy supplied from other degrees of freedom in the manner which has often been assumed in the discussion of thermal monomolecular reactions.[3] If such a process does occur, it is to be expected that the number of free radicals formed at such wave-lengths will increase rapidly with temperature whereas at the shorter wave-lengths which supply sufficient energy for direct dissociation such an effect will not be expected.

One method for the determination of the relative numbers of free radicals produced at different wave-lengths and temperatures depends upon the fact that such radicals catalyze a thermal decomposition of acetaldehyde by a chain process. As the temperature is raised these chains increase in length rapidly and account for practically all of the decomposition. At high temperatures, therefore, a determination of the ratio of the quantum yields at two wave-lengths constitutes a determination of the ratio of the concentrations of free radicals formed at those wave-lengths. If the measurements are carried out over a range of temperatures, the ratio of the quantum yields should remain constant as long as the chain process is the main reaction, and if there is no change in the efficiency of formation of radicals in the primary process. On the other hand, if a thermal contribution such as is mentioned in the preceding paragraph occurs at one wave-length and not at the other, a variation in the ratio of the quantum yields should be found. In this paper we shall present results on acetaldehyde with the wave-lengths 3132A and 2652A. The first lies in the region of discontinuous absorption whereas the second lies in a region of continuous absorption.

EXPERIMENTAL

The photolyses were carried out in a cylindrical fused quartz vessel five cm in diameter and 5.1 cm long with plane ends. This vessel was connected through capillary tubing with mercury "cut-offs" to a source of acetaldehyde, a manometer, an apparatus for the microanalysis of the gases, and the evacuating system. The reac-

* Presented at the symposium on "Kinetics of Homogeneous Gas Reactions." See page 725.

[1] T. G. Pearson and R. H. Purcell, J. Chem. Soc. 1151 (1935).

[2] J. Franck and K. Herzfeld, J. Phys. Chem. **41**, 97 (1937); M. Burton, J. Chem. Phys. **6**, 818 (1938).

[3] L. Kassel, *Kinetics of Homogeneous Gas Reactions* (Reinhold Publishing Co., New York, 1932), p. 73 *et seq.*

tion vessel was enclosed in an electric furnace which was set and regulated by hand to within ±0.5° of the desired temperatures. Temperatures were measured with the aid of a copper-constantan thermocouple fastened to the reaction vessel. Pressures were read to an accuracy of 0.01 cm on a mercury manometer with the aid of a cathetometer.

High vacuum technique was employed throughout. The pressure of foreign gases in the system before a run never exceeded the limit of detectability, about 10^{-5} mm.

Acetaldehyde was prepared from purified paraldehyde in the usual manner and stored at ice temperatures over anhydrous calcium sulfate and solid hydroquinone, the latter to remove any peroxides that might have been present.

The light source was an Hereaus quartz mercury arc. The light passed through a one-mm slit and was resolved into a spectrum by passing through a fused quartz system consisting of a lens to render the light parallel, a prism, and another lens which focused the spectrum on the slit used to select the desired wave-length. After passing this slit the light was made approximately parallel before passing through the reaction vessel by a lens set in one end of the furnace. The cross section of the light beam as it traversed the cell was 7.0 sq. cm. The intensity of the light was measured by means of a type 2 Weston photronic cell provided with a quartz window.

The optical system was calibrated for the determination of absolute quantum yields by irradiating acetaldehyde vapor at 30° with light of wave-lengths 3132 and 2652A under conditions of pressure and light intensity close to those used by Leighton and Blacet[4] in their experiments on the absolute quantum yields of decomposition of acetaldehyde. The eighth, ninth and tenth experiments listed in Table I give the results obtained in these calibration experiments. The quantum yields stated in parentheses are the values assumed for the conditions under which the experiment was carried out. Within rather wide limits, an error in the choice of quantum yields assumed for these experiments will not affect the conclusions to be drawn.

A quartz window in the rear of the furnace made it possible to measure directly the fraction of the incident light absorbed by the acetaldehyde even at elevated temperatures. A quartz water-filled cell placed between the exit window of the furnace and the photronic cell protected the latter from heat radiation. In all measurements with the photronic cell readings were taken alternately with and without clear glass filters of such composition that they absorbed completely the radiation for which the monochroma-

[4] P. A. Leighton and E. Blacet, J. Am. Chem. Soc., **55**, 1766 (1933).

TABLE I. *Quantum yields of decomposition of acetaldehyde.*

RUN	λ, A	T, °C	I_0 ERGS/SEC.	I_{ABS} ERGS/SEC.	I_{ABS} QUANTA $\times 10^{-16}$	(CH_3CHO) MOLES/CC $\times 10^{6}$	CO-PRODUCED MOLECULES $\times 10^{-18}$	γ_{OBS}	γ_{CORR}
1	2652	350	1238	322	2.62	3.36	15.40	588	584
2		300	1240	316	2.57	3.28	7.96	310	312
3		300	1240	319	2.59	3.31	8.30	320	321
4		200	1243	321	6.77	3.32	5.01	74.0	74.2
5		200	1230	310	10.05	3.24	6.87	68.4	69.0
6		100	1236	309	30.0	3.19	2.08	6.94	7.10
7		21	1234	342	70.7	3.61	0.653	0.92	0.92
8		30	1955	1574	153.9	16.97	1.262	(0.821)	
9		30	1957	1540	198.3	16.20	1.629	(0.821)	
10	3132	30	5225	2797	884	9.68	1.99	(0.225)	
11		350	1030	290	2.77	3.44	21.30	770	770
12		300	1062	291	2.76	3.22	11.6	420	450
13		200	1063	280	10.70	3.21	9.14	85.4	89.9
14		100	1073	268	38.45	3.04	2.44	6.35	6.90
15		60	1057	243	62.7	3.30	1.08	1.72	1.66
16		23	1063	247	70.8	3.36	0.27	0.38	0.38
17		300	4920	1363	6.54	3.39	12.9	197	433
18		300	3370	922	5.30	3.32	13.0	245	454
19		300	1416	396	3.79	3.41	14.5	383	452
20		300	1406	387	3.71	3.37	13.6	367	433
21		300	926	259	2.48	3.43	11.3	450	430

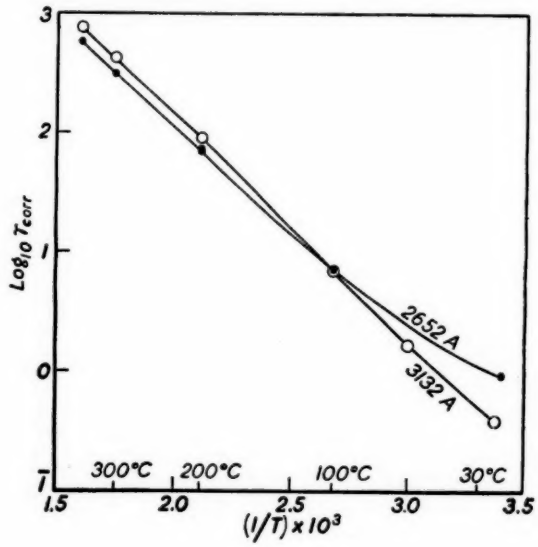

FIG. 1.

tor was set, yet transmitted most of the light of longer wave-length incident upon them. This procedure was adopted in order to eliminate errors from scattered visible light, toward which the photronic cell is particularly sensitive.

It may be noted here that the absorption coefficient found for λ3132 in acetaldehyde increased nearly 20 percent between room temperature and 300°. Since the incident light was not *strictly* monochromatic, this behavior probably does not have any theoretical significance. In order to compensate for fluctuations in the arc intensity a second photronic cell was mounted facing the quartz prism in such a way that it received a portion of the light beam (reflected from the front surface of the prism) through a Corex 986 filter. Under these conditions this photronic cell is affected principally by the mercury lines ~3660A, but this serves as an accurate control on the intensity of the 3132 line since the upper state for both lines is ^3D. It is not as good a control theoretically for the 2652A line but it was found to be a satisfactory indicator of the constancy of the arc conditions. By determining the ratio of simultaneous readings of the two photo-cells it was found possible to limit the readings during the photolyses to the control photo-cell thus reducing the probability of errors due to thermal effects in the photo-cell circuit.

The amount of decomposition was determined by freezing out the unchanged acetaldehyde with liquid air and pumping off the noncondensable gases with a Toepler pump. The amount of carbon monoxide in these gases was determined either by treatment with a bead of silver oxide or by heating with a bead of potassium hydroxide and cupric oxide. The average content of carbon monoxide for all except the room temperature runs was 49±0.3 percent in reasonable agreement with Leermakers.[5] The number of molecules of acetaldehyde decomposed was assumed equal to the number of molecules of carbon monoxide formed. Measurement of the pressure changes in some of the experiments made at 300° indicated that some polymerization also occurs. This is not surprising since it is well known that free radicals will catalyze polymerization.

The results obtained for the decomposition reaction at the wave-lengths 2652 and 3132A over a range from room temperature to 350°C are summarized in Table I and the logarithms of the corrected quantum yields are plotted against $1/T$ in Fig. 1. In the table the third column gives the temperature, the fourth, the light energy incident upon the acetaldehyde vapor in the cell, the fifth, the light energy absorbed by the vapor, the sixth, the total number of light quanta absorbed, the seventh, the average concentration of acetaldehyde vapor in the cell during the run (taking account of the slight decomposition occurring during the illumination), the eighth, the yield of CO obtained, the ninth, the observed quantum yield, and the tenth, a corrected quantum yield corresponding to that which should have been obtained if our "standard" conditions of concentration and light intensity had been exactly fulfilled. For standard conditions we have adopted a concentration of 3.36×10^{-6} mole/cc and a light intensity of 2.04×10^{-12} Einstein/sec./cc. A complete set of runs was carried out under conditions very close to these, and hence the corrections are very small. The corrections have been made by using the high temperature rate equation, $\gamma=k(CH_3CHO)/(I_{abs})^{\frac{1}{2}}$, given by Leermakers[5] and checked briefly by ourselves as regards the variation with light intensity. Ac-

[5] J. Leermakers, J. Am. Chem. Soc. **56**, 1537 (1934).

cording to this equation,

$$\gamma_{corr}=\left(\frac{I_{abs}}{2.04\times10^{-12}}\right)^{\frac{1}{2}}\times\frac{3.36\times10^{-6}}{(CH_3CHO)}\gamma_{obs}.$$

No correction has been applied to the room temperature runs since the reaction no longer follows the rate equation stated above. The work of Leighton and Blacet[4] shows, rather, that the quantum yields of decomposition at 3132A and at 2652A vary only slowly with changes in the pressure and light intensity.*

Fluorescence

No visible fluorescence could be detected at any temperature with $\lambda=2652$A as the exciting wave-length. With $\lambda=3132$A the fluorescence was readily visible at room temperature but decreased in intensity as the temperature was raised and was invisible at all temperatures above $\sim$150°C. The trend in the intensity as estimated visually is shown in Table II. These measurements were made at a constant concentration of 10.2×10^{-3} mole per liter of acetaldehyde.

Discussion

The data show that at high temperatures the quantum yields at the two wave-lengths are markedly different, the yield at 3132A being 30 percent greater than at 2652A. Since the conditions which determine the number of aldehyde molecules decomposed by a radical are identical for the two wave-lengths we must conclude that the number of chains started by the light, i.e., the number of free radicals produced, is greater with $\lambda=3132$A. The identity of the slopes of the $\log\gamma_{corr}$ *vs.* $1/T$ curves at the higher temperatures shows that under these conditions a change of temperature does not affect the number of radicals produced in the primary process or at least that it must produce the same effect at both wave-lengths.

At 300°C our results at $\lambda=3132$A are in reasonably good agreement with those of Leermakers,[5] his quantum yields being about ten percent less than ours under the same conditions of pressure and light intensity. At lower temperatures the results differ more markedly. This effect may be caused by a breaking down of Leermaker's rate law at lower temperatures since his work was done at constant pressure rather than at constant concentration of aldehyde. In our experiments at 3132A, as the temperature was dropped below $\sim$200°C and fluorescence began to appear, the quantum yield of decomposition decreased relative to that at 2652A and at 100°C the two quantum yields are approximately the same.

Below 100° the curve for the quantum yield at 3132A drops below that for 2652A and at room temperature the curves are still diverging. This behavior is understandable if we assume that at the higher temperatures the number of radicals formed from molecules excited by 3132A is increased with the aid of thermal energy whereas no such effect exists for those excited by 2652A. The observations on fluorescence are in accord with this view. No fluorescence is discernable with the shorter wave-length at any temperature, but with 3132A fluorescence is readily observed at room temperature and fades as the temperature is raised. This fading parallels in a rough manner the increase in quantum yield which is to be expected if the decrease in intensity is at least partially caused by an increase in the dissociation into radicals. The latter effect does not have to be the sole cause of the decrease in fluorescence as an increase in any other process such as a direct decomposition into methane and carbon monoxide will have a similar effect.

It is possible with the aid of the observations we have made to specify certain limits to the fraction of photoactivated molecules which decompose into free radicals. Obviously this fraction cannot exceed unity. Then the maximum

Table II. *Visual estimates of intensity of fluorescence of acetaldehyde vapor.* $\lambda=3132$A.

T, °C	Intensity
24	100%
66	80
104	35
124	15
136	8
220	<2
285	<2

* E. Blacet and D. Volman (J. Am. Chem. Soc. **60**, 1243 (1938)) drew the opposite conclusion regarding the change, with light intensity at 3132A, but an examination of their graph of γ *vs.* $1/(I_{abs})^{\frac{1}{2}}$ shows that a large (0.172) additive term has been overlooked.

yield of free radicals in the primary process at 2652A can be obtained from the difference between the two curves in Fig. 1 at temperatures above 200°C. The separation of the curves is determined by the ratio of the concentrations of the radicals during the irradiation and these concentrations are proportional to the square roots of the fractions of molecules which dissociate in the primary process. According to our curves the concentration of radicals produced at 3132A under these conditions is 1.32 times that produced at 2652A. The primary process is, therefore, 1.74 times as efficient in producing radicals. Since there is no reason to suppose that the efficiency of the primary process at 2652A increases with a decrease in temperature, we may conclude that not more than fifty-eight percent of the molecules activated by light of this wave-length decompose into radicals at any temperature.

The magnitude of the thermally produced increase in efficiency of the primary process at 3132A may be estimated if certain assumptions are made concerning the form the quantum yield *vs.* temperature curve would have in the absence of such an effect. Let us assume that the curve for $\lambda = 2652$A represents the "normal" form which would be followed at 3132A if there were no thermal contribution to the predissociation. A curve may be drawn through the point for 3132A at room temperature parallel to the 2652A curve. The difference between this curve and the observed values at high temperatures corresponds to a difference of a factor of 3.4 in the concentration of radicals during the irradiation or a factor of 11.5 in the efficiency of the primary processes. This estimate gives the maximum increase attributable to thermal effects between room temperature and say, 300°. An estimate of the minimum effect can be made by a linear extrapolation of the high temperature portion of the curve to room temperature and taking the difference between extrapolated and observed points. The difference corresponds to a change in the concentration of radicals of 1.45 or a change in the primary process of 2.1. This value must be considered as a minimum since the true curve in the absence of a thermal effect probably resembles the 2652A curve more closely than it does a straight line.

The fact that the light quanta of greater energy were less efficient in producing free radicals at high temperatures was quite unexpected. However, the experimental result is unambiguous. Usually it has been assumed that shorter wave-lengths are more efficient in producing radicals. In this case it is probable that the light of $\lambda = 2652$A excites the molecule to a different electronic state which dissociates into free radicals less readily.

Discussion

R. A. Ogg, Jr., *Stanford University:* Are the absorption coefficients of acetaldehyde for λ3132 and 2654A significantly different? If not, there is possibility of a different distribution of radiant density. Since the rate expression involves the square root of the rate of energy absorption per unit volume, in the case of long chains this could lead to an apparent difference in quantum efficiency.

G. K. Rollefson, *University of California:* The absorption coefficients are nearly the same. We were actually working with the same absorption density in the two cases.

D. C. Grahame, *University of California:* The reaction cell was relatively short,—only 5 cm long.

W. A. Noyes, Jr., *University of Rochester:* Might not the fluorescence at 3132A be due to biacetyl?

G. K. Rollefson, *University of California:* We considered carefully the possibility that biacetyl might be a factor in fluorescence. However the fluorescence is observed as soon as the light is turned on, and it doesn't change with time.

W. A. Noyes, Jr., *University of Rochester:* Acetone fluorescence increases with time but it does not seem to be zero at the start of irradiation. This matter is being investigated at present.

G. K. Rollefson, *University of California:* You will have to assume that an extremely small

amount of biacetyl will give an intense fluorescence.

D. C. Grahame, *University of California:* If it is biacetyl it must be fluorescing as it is formed.

Milton Burton, *New York University:* If the potential energy relationship already shown for acetaldehyde[6] is considered it is seen that the interesting results obtained by Rollefson and Grahame are readily explained in the light of some earlier suggestions.[7] At the wave-lengths used there is only one excited electronic state from which the molecule may dissociate. The first process results in a slow decomposition in the same hypersurface into two ultimate molecules in the primary act; i.e., CH_4 and CO. This reaction (apart from fluorescence or molecular deactivation) occurs exclusively when the energy in the photon absorbed is insufficient to break the C—C bond and to produce free radicals. When a sufficient amount of energy is absorbed the molecule may dissociate by transition from the excited state to a weakly attractive state which crosses the former along a hyperline. Rollefson and Burton have shown that under such conditions the probability of a free radical decomposition is highest when the amount of energy contained by the molecule in the excited state is a minimum in excess of that required to cause that type of decomposition. Thus, an increase of temperature when light of 2652A is used decreases the free radical yield. On the other hand, 3132A is insufficient to decompose acetaldehyde into free radicals without the contribution of thermal energy from the vibrational degrees of freedom. Thus, an increase in temperature increases the probability that the molecule excited with 3132A executes an oscillation which crosses the intersection of the hypersurface corresponding to the excited state and the weakly attractive hypersurface corresponding to free radical production. It is interesting that the same considerations lead to the conclusion that a wave-length considerably less than 2652A, for example 2537A, will lead to decreased free radical production. I am informed by Professor Leighton that results indicating such a phenomenon have been observed in his laboratory. This model suggests that when the logarithm of the quantum yield is plotted against temperature as in Fig. 1, the 3132A line does not run parallel to the 2652A line but eventually joins it at higher temperatures. Such an effect, however, is not observed in Fig. 1.

G. K. Rollefson, *University of California:* This explanation is all right with light of 3132A, but there are difficulties in applying it to short wave-lengths. In my opinion, the absorption spectrum of acetaldehyde indicates quite definitely that there are two different electronic states. One corresponds to complete absorption and the other gives rise to a definite structure in the spectrum. I am basing these statements on observations made by Professor Leighton a few years ago. If one separates the two states and draws potential energy curves one finds overlapping. With two electronic states it is not surprising that there may be some differences in properties.

J. G. Winans, *University of Wisconsin:* The failure to obtain fluorescence at 2652A but not at 3132A as well as the increase in efficiency for dissociation with temperature at 3132A in comparison to 2652A excitation could be accounted for if the potential energy curves are like those of iodine. For example, if 2652A produced dissociation and 3132A produced stable molecules whose vibration energy was near the dissociation limit, then an increase in temperature would increase the efficiency of dissociation by 3132A but not that by 2652A excitation.

K. F. Herzfeld, *Catholic University of America:* The difficulty is that according to this view you should expect greater efficiency in the short wave-length. I also have difficulty in accepting Dr. Burton's explanation because, according to it, one should expect to have intense fluorescence at 2632A, for in this case the molecule undergoes internal vibrations for a considerable time before going into the CH_4 state.

D. C. Grahame, *University of California:* There is no fluorescence of the short wave-length at any temperature.

[6] H. A. Taylor and M. Burton, J. Chem. Phys. **7**, 414 (1939).
[7] G. K. Rollefson and M. Burton, J. Chem. Phys. **6**, 674 (1938).

M. Burton, *New York University:* Professor Davis and I have given further consideration to the nature of the hypersurfaces involved and have arrived at conclusions which incorporate the suggestion made by Professor Rollefson and which, we think, satisfy Professor Herzfeld's criticism. Our conclusions will be published shortly.

P. A. Leighton, *Stanford University:* Dr. Volman at Stanford University has obtained some results which may be of interest here. He has observed the rates of removal of tellurium mirrors in a Paneth apparatus, using different wave-lengths on acetone and acetaldehyde. When the intensities were adjusted to give the same rates of formation of noncondensable gaseous products, the following relative rates of mirror removal were observed:

	Acetone	Acetaldehyde
3160–80A	1.06	1.0
2800	3.6	1.5
2537	10.8	—

The gases were irradiated at room temperature, the pressure was 1.5 mm, the streaming velocity 8 meters/sec., the tube diameter 10 mm, and the distance from the point of irradiation to the mirror 90 mm. Taking the rate of mirror removal as proportioned to the number of radicals produced, the 50 percent increase in going from 3160 to 2800 in acetaldehyde at room temperature should be compared with the results of Gorin, who from the rate of CH_3I formation in acetaldehyde-iodine mixtures concluded that at temperature above 100°C more radicals are produced at longer wave-lengths. These unexpected results are explained by Professor Rollefson's suggestions. The increase in the rate of mirror removal with decreasing wave-lengths in acetone is remarkable, as was the behavior of acetaldehyde at 2537A. At this wave-length in the streaming system no mirror removal and no gaseous products could be detected with pure acetaldehyde. For comparison, acetone removed mirrors and gave products at 2537A, acetaldehyde did so at 2800A and at 2537A in the presence of mercury vapor, and in a static system at the same pressure it gave products with 2537A both in presence and absence of mercury vapor.

The Cadmium Photosensitized Reactions of Ethane *

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An investigation of the cadmium photosensitized reactions of ethane has been made. It is concluded that the primary process is a C−H bond split, probably by the reaction

$$Cd(^3P_1)+C_2H_6=CdH+C_2H_5.$$

The products of the reaction are hydrogen, methane, propane, butane, and higher hydrocarbons. The methane probably largely results from methyl radicals produced by

$$H+C_2H_5=2CH_3,$$

and the higher hydrocarbons from recombination reactions of radicals. Two experiments have also been made on the decomposition of propane and butane.

INTRODUCTION

THE investigation of mercury photosensitized reactions has proved to be of great interest, since this method makes it possible to endow the reactant molecule with a definite and reproducible amount of energy. In the case of organic decomposition reactions, free radicals are usually produced in the process, and the method therefore gives results of special interest in connection with the rates of elementary reactions.[1, 2]

In the mercury photosensitized reactions of the hydrocarbons there are three main possibilities for the primary step, *viz.* the rupture of a C−C bond, the rupture of a C−H bond, and the dissociation into atoms of hydrogen produced from the decomposition of the hydrocarbon. These processes require, respectively, about 70–80 kcal., 90–100 kcal., and 103 kcal. The $Hg(6^3P_1)$ excitation energy is 112 kcal., which makes all three processes possible. Considering the importance of the information which has been derived from mercury photosensitization experiments, it is obviously of interest to investigate photosensitized reactions in which the energy input is of a different magnitude. Three metals which have sufficiently high vapor pressures at moderate temperatures to be feasible sensitizers are sodium, cadmium, and zinc.

Experiments on sodium photosensitization have been made by Jungers and Taylor,[3] but in view of the small excitation energy of the sodium D line (48 kcal.), no effect could be produced with saturated hydrocarbons. Cadmium and zinc, with $^3P_1$ levels 87 and 92 kcal. above the ground state, respectively, obviously offer much more interesting possibilities.

No previous work has been done on zinc photosensitization, and only a brief investigation of cadmium photosensitization has been made. Bates and Taylor[4] reported that in ethylene-hydrogen-cadmium vapor mixtures illuminated with λ3261 no hydrogenation to ethane occurred, but that some of the ethylene was polymerized. They showed, however, that hydrogen quenched the resonance radiation, and suggested that it took up the energy of the excited cadmium atom as vibrational energy. (Hydrogen has a vibrational level at about 88.7 kcal.) Bender[5] has investigated the quenching of cadmium resonance radiation by hydrogen. He detected the CdH band spectrum during the process, and suggests that the quenching process is

$$Cd+H_2=CdH+H-88 \text{ kcal.}$$

The quenching of cadmium resonance radiation by hydrogen and a number of other gases has been investigated by Lipson and Mitchell.[6]

* Presented at the symposium on "Kinetics of Homogeneous Gas Reactions." See page 725.
** Holder of a Studentship from the National Research Council of Canada.
[1] H. S. Taylor, Third Report of the Committee on Photochemistry of the National Research Council (U. S. A.), J. Phys. Chem. **42**, 763 (1938).
[2] E. W. R. Steacie, Chem. Rev. **22**, 311 (1938).
[3] J. C. Jungers and H. S. Taylor, J. Chem. Phys. **4**, 94 (1936).
[4] J. R. Bates and H. S. Taylor, J. Am. Chem. Soc. **50**, 771 (1928).
[5] P. Bender, Phys. Rev. **36**, 1535 (1930).
[6] H. C. Lipson and A. C. G. Mitchell, Phys. Rev. **48**, 625 (1935).

Further investigation of cadmium and zinc photosensitized reactions should be of considerable interest, and such investigations have been delayed only because of the lack of suitable light sources. Recently convenient cadmium and zinc resonance lamps of high intensity have been developed,[7, 8] and we hope to carry out a comprehensive investigation of the photosensitized reactions.

The present investigation deals with the cadmium photosensitized reactions of ethane, which should be of interest by comparison with the corresponding mercury photosensitized reactions.[9–15] There seems to be no doubt that the primary step in the mercury photosensitized reaction is[14, 15]

$$Hg(^3P_1)+C_2H_6=C_2H_5+H+Hg(^1S_0).$$

Experimental

The light source

The lamp-reaction vessel system has been previously described.[7] The lamp consisted of a spiral of 7-mm Corex D tubing, the ends of which were joined to Pyrex tubes, into which were sealed standard neon sign "coated" electrodes. The lamp contained a small pellet of cadmium, together with 3 mm pressure of neon as a carrier gas. It was outgassed, filled, etc. by the usual neon sign technique. The lamp operated from a 6000-volt sign transformer, and was run on about 100 milliamperes.

A Pyrex reaction vessel, 9 cm in a diameter and 19 cm long, was sealed directly to the lamp, only the electrode chambers remaining outside. The vessel was provided with two connections for the circulation of gases, a thermocouple well, and a Corex D window to permit spectroscopic examination of the light, intensity measurements, etc. The entire lamp-reaction vessel system, including the electrode chambers, was placed in an electric furnace which was thermostatically controlled, and was maintained at a temperature of 280°C.

With the original lamp occasional fluctuations in intensity occurred. Since diminutions in the intensity of the cadmium resonance radiation were accompanied by an increase in the intensity of the visible neon spectrum, it was evident that the cause was a drop in the amount of cadmium vapor in the discharge. To offset this, both electrode chambers were wound with a spiral of $\frac{1}{16}$-inch bore copper tubing. During the operation of the lamp a slow stream of compressed air was blown through the coil on one electrode, thus cooling it and causing a slow steady diffusion of cadmium vapor through the discharge. After about 24 hours operation, the cooling was applied to the other electrode instead, and the cadmium was thus distilled back. Under these circumstances the output of the lamp was much more reproducible, and never varied by more than about 2 percent.

The total emission of the lamp was estimated in two ways. (a) The light emitted through the window was measured by means of a thermopile and a system of filters, and the total output was estimated by a geometrical calculation. This gave only a very rough estimate. (b) The output was estimated actinometrically by measuring the rate of the unsensitized acetone photolysis. The quantum yield of the acetone photolysis may be taken as unity at 280°C.[16] The reaction was followed by measuring the production of carbon monoxide. The mean rate of carbon monoxide formation was found to be 9.4×10^{-8} mole per sec. The absorption of light by acetone has been investigated by Porter and Iddings.[17] The absorption is very small above 3300A, and hence the only appreciable absorption is that of the resonance line. From Porter and Idding's data, and a geometrical estimate of the mean light path, it was found that the absorption should be 3.1 percent at the acetone pressures used. Whence we obtain for the output of the lamp 3.1×10^{-6} Einstein per sec. This value is

[7] E. W. R. Steacie and R. Potvin, Can. J. Research **B16**, 337 (1938).
[8] E. W. R. Steacie and H. Habeeb, unpublished.
[9] S. Tolloczko, Przemysl Chem. **11**, 245 (1927).
[10] H. S. Taylor and D. G. Hill, J. Am. Chem. Soc. **51**, 2922 (1929).
[11] W. Kemula, Roczniki Chem. **10**, 273 (1930).
[12] Kemula, Mrazek and Tolloczko, Coll. Czech. Chem. Comm. **5**, 263 (1933).
[13] E. W. R. Steacie and N. W. F. Phillips, J. Chem. Phys. **6**, 179 (1938).
[14] E. W. R. Steacie and N. W. F. Phillips, Can. J. Research **B16**, 303 (1938).
[15] Steacie, Alexander and Phillips, Can. J. Research **B16**, 314 (1938).
[16] C. A. Winkler, Trans. Faraday Soc. **31**, 761 (1935).
[17] C. W. Porter and C. Iddings, J. Am. Chem. Soc. **48**, 40 (1926).

uncertain owing to (a) uncertainties in the absorption coefficient of acetone, (b) the possibility of the absorption coefficient changing with temperature, and (c) to the uncertain length of the light path. However, it is felt that the estimate cannot be out by more than a factor of 2. A second light source was also used during the investigation, which had a somewhat higher output, *viz.* 5.2×10^{-6} Einstein per sec.

Table I illustrates the characteristics of one of the sources. The efficiency is quite high, being within one power of 10 of that of the most intense commercial mercury lamps. The data in Table I refer to λ3261 only. The relative intensities of the other wave-lengths were determined spectrographically, and were found to be

3261A	100
3404	4
3466	19
3613	21
4678	14
4800	14

The reaction system

The reaction system was similar to one which had been used previously in mercury photosensitization experiments.[13] The gases were circulated by a magnetically operated pump through the lamp-reaction vessel system, and then through a cooled trap to remove products of higher molecular weight, and thus cut down secondary reactions. The gases then passed through a cadmium saturator containing a large surface of cadmium-tin alloy. This was maintained at a temperature of 290°C. The reaction mixture then passed back to the reaction vessel again. The saturator and the furnace containing the reaction vessel adjoined one another, so that there was no cold tubing between them. No appreciable deposition of cadmium in the reaction vessel occurred.

TABLE I. *Characteristics of resonance lamp.*

CURRENT, MILLIAMP.	VOLTAGE	INPUT, WATTS	OUTPUT, EINSTEINS/SEC.	OUTPUT, WATTS	EFFICIENCY
112	458	52	3.1×10^{-6}	1.15	2.2%
90	490	44	2.7	1.0	2.2
60	540	32	2.1	0.75	2.3
50	575	28	1.8	0.67	2.4

The reaction system was also provided with a connection to a McLeod gauge and mercury vapor pump, storage vessels for gases, a mercury manometer, and an outlet through which samples of gas could be removed for analysis.

Analysis

The products of the reaction were pumped by means of a Toepler pump into a portable mercury gas-holder. They were then transferred to a small-capacity low temperature distillation apparatus of the Podbielniak type. In this apparatus methane and hydrogen were taken off as a single fraction and analyzed by combustion. Tests on all fractions were also made for unsaturated hydrocarbons by conventional methods in a Burrell gas analysis apparatus.

Materials

Ethane was secured in cylinders from the Ohio Chemical and Manufacturing Company. Analysis showed it to contain from 1 to 2 percent ethylene, less than 0.3 percent of hydrogen plus methane, and less than 0.3 percent of higher hydrocarbons. The cylinder gas was purified by passage through a 60-cm tube containing copper oxide at 300°C, through saturated bromine water into a two-liter bottle which was strongly illuminated, through a 40-percent solution of potassium hydroxide, and finally through a trap at −80°C to remove water. It was then condensed by means of liquid air into small high pressure cylinders fitted with needle valves. The resulting gas contained no impurities which could be detected with the analytical method used.

Hydrogen was obtained from commercial cylinders, and was purified by passage over hot platinized asbestos, followed by a liquid-air trap.

Cadmium was of C.P. grade, and was purified by distillation.

Acetone was reagent grade, obtained from the Eastman Kodak Company.

Propane, butane, and ethylene were obtained in cylinders from the Ohio Chemical and Manufacturing Company. They were stated to be 99 percent pure, and were further purified by fractional distillation.

TABLE II. *Absorption of resonance radiation. Temperature = 278°C. Cadmium vapor pressure = 0.018 mm. Distance from source to exit window = approximately 7.5 cm.*

Ethane							
Pressure, mm	0.5	1.0	1.5	2.0	3.0	6.0	100
% absorption	14	32	44	60	85	91	97
Hydrogen							
Pressure, mm	0.5	1.0	2.0	4.0	16.0	21.0	42.0
% absorption	48	61	71	78	89	97	97
Propane							
Pressure, mm	0.5	1.0	1.5	2.0	5.0	12.0	45.0
% absorption	56	70	80	87	89	91	97
Butane							
Pressure, mm	0.3	1.0	1.5	4.0	9.0	30.0	50.0
% absorption	63	72	76	88	92	94	97
Ethylene							
Pressure, mm	1.0	2.0	3.0	4.0	8.0	42.0	
% absorption	85	93	98	99	99	98	
Acetone							
Pressure, mm	1.0	2.0	3.0	4.0	8.0	40.0	
% absorption	32	48	56	59	61	72	

THE ABSORPTION OF CADMIUM RESONANCE RADIATION

To determine with certainty the fate of the absorbed radiation, it is necessary to know the details of the quenching processes involved. In the case of cadmium resonance radiation no information is available on the quenching by the hydrocarbons other than methane. In the absence of such knowledge, however, considerable information can be obtained by measuring the "absorption" of the resonance radiation in the presence of foreign gases.

In the present case this was done by two methods: (a) spectrophotometrically, using a small Hilger quartz spectrograph and (b) by measuring the light emitted through the window of the reaction vessel by means of a Weston photronic cell with a quartz window, using a Red Purple Corex filter to cut out the visible radiation. In this way it was possible to measure the intensity of the resonance line (3261A) plus the neighboring lines (3404, 3466, 3613). The relative intensities of the latter were small, and were estimated spectrographically, and hence the intensity of the resonance radiation could be inferred directly from a reading of the photronic cell. In this way the absorption of the resonance radiation was determined in the presence of hydrogen, ethane, and other gases. The results are given in Table II. It should be emphasized that the above data are by no means equivalent to true quenching efficiencies. However the data do seem to indicate more efficient "absorption" than in the case of mercury vapor. This is undoubtedly to be ascribed to the much longer life of the $^3P_1$ cadmium atom as compared with mercury. The data should also serve to give a qualitative estimate of the relative amounts of energy transferred to the different components in a mixture of gases, such as exists after the products of reaction have begun to accumulate.

THE CADMIUM PHOTOSENSITIZED DECOMPOSITION OF ETHANE

In the first experiments with ethane, the trap was left at room temperature, and no attempt was made to remove the products of the reaction during a run. The results are given in Tables III and IV.

As may be seen from Tables III and IV, and from Fig. 1, the indications are that hydrogen is the main product at short exposure times. With increasing reaction time the percentage of hydrogen diminishes and that of methane increases. At the same time the quantity of propane diminishes, and products of higher molecular weight are formed.

In an attempt to prevent secondary reactions, experiments were made at low trapping temperatures. The results are given in Tables V and VI. It will be seen that the inhibition of secondary processes was only partially successful. This is apparently due to the fact that even at the lowest trapping temperatures employed propane

TABLE III. *The decomposition of ethane. Volume of system 2480 cc. Temperature of reaction vessel 278°C. Cadmium vapor pressure 0.018 mm. Circulation rate 1800 cc. per min. Resonance radiation 5.2×10^{-6} Einstein per sec. Temperature of trap—Room temperature.*

RUN NO.	TIME, MIN.	INITIAL PRESSURE, MM	FINAL PRESSURE, MM	DECOMPOSITION, MOLES PER SEC. $\times 10^6$	QUANTUM EFFICIENCY
1	30	203	204	1.6	0.31
2	30	203	204	1.5	0.30
3	30	203	203	1.4	0.29
4	60	203	203	1.4	0.29
5	120	203	205	1.2	0.23
6	180	203	204	1.0	0.19
7	300	203	204	0.9	0.18
8	360	203	203	0.8	0.15
9	420	203	203	0.0	—
	Blank run—lamp off				

and butane still have appreciable vapor pressures. Since the trapping involves a reduction in the partial pressure of ethane, it increases the chance of reaction of whatever propane and butane remain in the gas phase. Further, from the results of the absorption experiments it appears that propane and butane are more efficient than ethane in quenching the resonance radiation.

The Cadmium Photosensitized Reactions of Ethane-Hydrogen Mixtures

It is apparent from the foregoing results that hydrogen is the main initial product of the reaction, but that its production is greatly diminished in the later stages of the reaction, except at low trapping temperatures. To investigate the point further, runs were made with ethane-hydrogen mixtures. The results are given in Tables VII and VIII.

The main features of the above results are the large production of methane, and the fact that hydrogen is still produced, although in much smaller amounts than before. It seems probable that reactions of hydrogen atoms are the main processes here, since hydrogen appears to be more efficient than ethane in quenching the resonance radiation.

The Decomposition of Propane and Butane

Since secondary reactions of propane and butane are coming into play in the experiments with ethane, it is desirable to have some information about the cadmium photosensitized reactions of these substances. Two runs were therefore made with propane and butane, the results of which are given in Tables IX and X. These results are to be considered as qualitative only, pending further work, but they should at least show the main features of the reactions.

Table IV. *The products of the ethane decomposition. Experimental conditions as in Table III.*

Run No.	Gaseous products, mole percent				Higher Products
	H_2	CH_4	C_3H_8	C_4H_{10}	
1	51.9	9.1	39.0	—	Small with low times of exposure, increasing with exposure time. Mainly hexane.
2	49.0	9.0	42.0	—	
3	64.1	11.7	24.2	—	
4	59.0	20.0	21.0	—	
5	42.5	35.0	16.5	6.0	
6	38.0	48.5	7.7	5.8	
7	28.1	66.3	—	5.6	
8	19.2	65.7	4.9	10.2	
9	0.0	0.0	0.0	0.0	

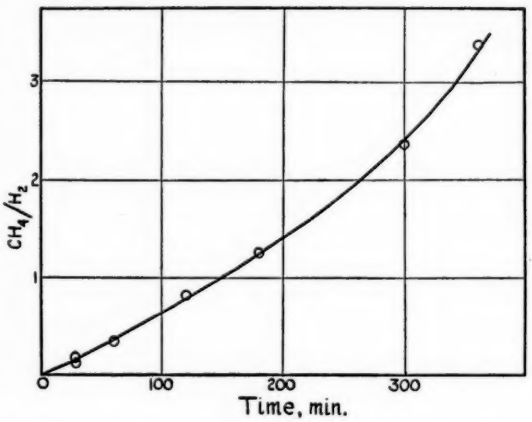

Fig. 1. Variation of methane-hydrogen ratio with reaction time.

Discussion

The ethane decomposition

The foregoing results show that in the early stages of the reaction the hydrogen production is very large, while that of methane is small. It therefore appears certain that the primary

Table V. *The decomposition of ethane at low trapping temperatures. Resonance radiation 3.1×10^{-6} Einstein per sec. Other conditions as in Table III.*

Run No.	Time, min.	Temperature of trap	Partial pressure of ethane	Fraction of ethane decomposed	Quantum efficiency
1	60	−124°C	68 mm	0.23	0.45
2	90	−115	150	0.50	0.39
3	240	−125	62	0.93	0.31
4	360	−125	62	0.96	0.22

Table VI. *The products of the ethane decomposition at low trapping temperatures.*

Run No.	Gaseous products, mole percent					Liquid products, expressed as weight percent of total products
	H_2	CH_4	C_3H_8	C_4H_{10}	C_2H_4	
1	42.4	12.0	40.0	2.6	1.0	5
2	45.8	18.7	35.5		—	Not determined
3	40.9	27.7	23.8	7.0	0.7	13
4	45.5	33.5	11.6	8.9	0.5	20

TABLE VII. *The decomposition of ethane-hydrogen mixtures. Initial ethane pressure 100 mm. Initial hydrogen pressure 100 mm. Final pressure 200±2 mm. Resonance radiation 5.2×10^{-6} Einstein per sec. in runs 1–3; 3.1×10^{-6} Einstein per sec. in runs 4–6. Other conditions as in Table III.*

Run No.	Trap Temperature	Time, min.	Decomposition Rate, moles per sec. $\times10^{6}$	Quantum Efficiency
1	25°C	60	0.8	0.16
2	25	120	0.7	0.14
3	25	240	0.7	0.14
4	−125	60	1.3	0.42
5	−125	120	1.1	0.34
6	−125	180	0.9	0.29

step involves a C−H bond split, as in the case of the mercury photosensitized reaction. There are two ways in which this might come about, *viz.*

$$C_2H_6+Cd(^3P_1)=C_2H_5+H+Cd(^1S_0) \quad (1)$$

and

$$C_2H_6+Cd(^3P_1)=C_2H_5+CdH. \quad (2)$$

Since the formation of cadmium hydride has been shown to occur in the presence of hydrogen, it is obviously possible for it to be formed here. If the reaction occurs by (1), the energy available to split the C−H bond is the excitation energy of the cadmium atom, 87 kcal., plus a certain amount of kinetic energy. Estimates of the C−H bond strength vary greatly,[18] ranging from 92 to 108 kcal. The values are uncertain, however, and reaction (1) may therefore be possible. Since the heat of formation of CdH from the atoms is 15.3 kcal., reaction (2) would be possible provided that the strength of the C−H bond is not much over 102 kcal., and (2) therefore appears to be the most likely primary step. However, in view of the uncertainty in the bond strength, no definite conclusion can be drawn at present.

Since little methane is formed in the early stages of the reaction, it appears certain that methane formation is not the result of the possible primary step

$$Cd(^3P_1)+C_2H_6=Cd(^1S_0)+2CH_3. \quad (3)$$

The main possibilities for methane formation are therefore

$$H+C_2H_6=CH_4+CH_3, \quad (4)$$

$$H+C_2H_5=2CH_3. \quad (5)$$

Taylor has discussed[1] the relative probabilities of reactions (4) and (5), and has concluded that reaction (5) probably is of much more importance than (4) as a source of methyl radicals. Recent work of Steacie and Parlee[19] furnishes strong confirmation of this, and it may therefore be concluded that methane formation occurs by (5), followed by

$$CH_3+H=CH_4 \quad (6)$$

and

$$CH_3+H_2=CH_4+H. \quad (7)$$

Estimates of the activation energy of the latter reaction vary,[2] but it should be of some importance at 280°C. It is possible that some methane formation also occurs by

$$CH_3+C_2H_6=CH_4+C_2H_5. \quad (8)$$

This reaction is slow at room temperature, but appreciable at 160°C,[20] and may therefore be important at 280°C.

The higher hydrocarbons presumably result from the recombination of radicals by reactions such as

$$CH_3+C_2H_5=C_3H_8, \quad (9)$$

$$2C_2H_5=C_4H_{10}, \quad \text{etc.} \quad (10)$$

The yield of propane is very high in the early stages of the reaction. This differs from the

TABLE VIII. *The products of the decomposition of ethane-hydrogen mixtures.*

Run No.	Gaseous products, mole percent					Liquid products, expressed as weight percent of total products
	H_2	CH_4	C_3H_8	C_4H_{10}	C_2H_4	
1	13.2	73.0	13.8	—	—	Considerable,
2	9.3	70.0	17.2	3.5	—	but not deter-
3	7.2	75.2	6.9	10.7	—	mined quanti-
						tatively.
4	5.8	60.6	25.4	8.2	—	5
5	26.1	40.8	8.9	24.2	—	10
6	23.2	50.0	10.0	16.8	—	11

[18] See G. K. Rollefson and M. Burton, *Photochemistry* (Prentice-Hall, New York, 1939).

[19] E. W. R. Steacie and N. A. D. Parlee, Paper presented at Faraday Society Symposium on Hydrocarbon Chemistry, April, 1939.

[20] J. P. Cunningham and H. S. Taylor, J. Chem. Phys. **6**, 359 (1938).

results obtained in mercury photosensitization experiments, where much methane is obtained at all stages and relatively small amounts of propane. This is probably due to the following circumstances. There are three main fates of a methyl radical, *viz.* combination with a hydrogen atom to form methane, with an ethyl radical to form propane, or with another methyl radical to regenerate ethane. The third possibility will merely decrease the quantum yield, and will not affect the products of the reaction. At the higher temperatures involved in the present work, reactions (5) and (6) will keep the concentration of hydrogen atoms down to a much lower value. As a result (9) will be much more important than (6), and the production of propane will thus be much greater than in the case of mercury photosensitization experiments at room temperature. In the presence of hydrogen the concentration of hydrogen atoms increases on account of the occurrence of (11), and hence the methane production is higher and that of propane is lower.

The decrease in the relative amount of hydrogen as compared with methane in experiments of long duration is probably partly due to reaction (5). It should be noted, however,

TABLE IX. *The cadmium photosensitized decomposition of propane.*

Trap temperature	25°C
Resonance radiation	3.1×10^{-6} Einstein/sec.
Reaction time	120 min.
Initial pressure	157 mm
Final pressure	158 mm
Fraction of propane decomposed	0.40
Quantum efficiency	0.28
Other conditions as in Table III.	

Gaseous products, mole percent

H_2	6.4
CH_4	67.4
C_2H_4	0.6
C_4H_{10}	25.6

Liquid products 28.1 percent by weight of the total products.

that at no stage of the reaction is hydrogen actually consumed. Its rate of formation merely decreases relative to that of methane, and hence its percentage in the products diminishes. This is undoubtedly due to secondary reactions of propane and butane, since as shown by Tables IX and X, these decompositions result in a large formation of methane and virtually no hydrogen. In support of this may be cited the fact that in experiments at low trapping temperatures, where the secondary reactions are cut down, the percentage of hydrogen in the products does not diminish appreciably as the run progresses. In these runs the methane increases at the expense of the propane and butane, and liquid products are formed. It may be noted that the quantum efficiency of the ethane decomposition is higher in experiments at low trapping temperatures, since less of the incident energy is being consumed by secondary processes.

TABLE X. *The cadmium photosensitized decomposition of butane.*

Trap temperature	25°C
Resonance radiation	3.1×10^{-6} Einstein per sec.
Reaction time	115 min.
Initial pressure	202 mm
Final pressure	202 mm
Fraction of butane decomposed	0.30
Quantum efficiency	0.29
Other conditions as in Table III.	

Gaseous products, mole percent

H_2	0.6
CH_4	24.2
C_2H_6	28.8
C_3H_8	46.4

Liquid products 58.2 percent by weight of the total products.

The large production of hydrogen here is also to be contrasted with the results of mercury photosensitization experiments at room temperature, where the stationary hydrogen concentration in a circulating system at low trapping temperatures is very low, and that of methane is high.[13] This may be due to relative inefficiency of (11).

The reaction in the presence of hydrogen

In the presence of hydrogen there is a very large production of methane, and hydrogen is still produced, although in much smaller amount than before. In the presence of hydrogen another primary reaction comes into play, *viz.*

$$Cd(^3P_1)+H_2=CdH+H. \qquad (11)$$

In view of the very efficient quenching of cadmium resonance radiation by hydrogen, it is apparent that in a 1 : 1 hydrogen-ethane mixture the hydrogen is absorbing most of the energy, either by (11), or possibly by

$$Cd(^3P_1)+H_2=Cd(^1S_0)+H_2^*. \qquad (12)$$

Reaction (11) must then be followed by second-

ary reactions of hydrogen atoms, such as

$$H+C_2H_6=C_2H_5+H_2. \quad (13)$$

This is known to have a low activation energy.[13,14] The large yield of methane is evidently due to the increased occurrence of (5) on account of the greatly increased hydrogen atom concentration.

The decomposition of propane and butane

The main reactions of propane are presumably of the same type as ethane, *viz.*

$$\left.\begin{aligned} C_3H_8+Cd(^3P_1)&=C_3H_7+H+Cd(^1S_0)\\ \text{or}\qquad &=C_3H_7+CdH \end{aligned}\right\}, \quad (14)$$

$$H+C_3H_7=C_2H_5+CH_3, \quad (15)$$

$$C_3H_7=C_2H_4+CH_3, \quad (16)$$

$$2C_3H_7=C_6H_{14}, \text{ etc.} \quad (17)$$

The occurrence of reaction (15) appears to be well established by the work of Steacie and Parlee[19] on the reaction of hydrogen atoms, produced by the discharge-tube method, with propane. The propyl radical is known to be unstable at high temperatures, and ethylene formation undoubtedly results from (16). However, preliminary experiments on the cadmium photosensitized hydrogenation of ethylene show that this reaction occurs very rapidly, and hence little ethylene survives in the products.

These results are to be contrasted with recent experiments of Steacie and Dewar[21] on the mercury photosensitized decomposition of propane. Their results indicate that the reaction is almost exclusively

$$Hg(^3P_1)+C_3H_8=C_3H_7+H+Hg(^1S_0), \quad (18)$$

$$2C_3H_7=C_6H_{14}. \quad (19)$$

However, their work was done at room temperature, where the propyl radical is stable, whereas here the instability of the propyl radical makes a profound change in the products of the reaction.

The reactions of butane appear to be similar to those of propane.

In conclusion it should be emphasized that the present work is to be regarded as exploratory in nature, and that much further work is needed on these reactions.

The authors wish to express their indebtedness to the National Research Council of Canada for financial assistance.

[21] E. W. R. Steacie and D. J. Dewar, unpublished.

Discussion

W. A. Noyes, Jr., *University of Rochester:* I would like to ask whether the cadmium line which comes at 2300A was removed.

E. W. R. Steacie, *McGill University:* Yes, the construction of the lamp is such that this line is completely absent.

W. A. Noyes, Jr., *University of Rochester:* Do you get the emission of the Cd−H band?

E. W. R. Steacie, *McGill University:* I can't say absolutely. Careful quantitative measurements will be necessary to decide.

K. F. Herzfeld, *Catholic University of America:* I would like to ask whether experiments could be made at higher temperatures. If so, it would be possible to investigate subsequent changes.

E. W. R. Steacie, *McGill University:* There wouldn't seem to be any difficulty in the case of ethane. The Corex glass doesn't stand up at temperatures above 400°.

J. G. Winans, *University of Wisconsin:* Was an inert gas used in the lamps?

E. W. R. Steacie, *McGill University:* Actually the lamps run on 3 mm neon. We wound a copper spiral on each electrode and blew compressed air through each one alternately, to cool it. In this way the cadmium is circulated by vaporization.

Chemical Activation by Gaseous Ionization*

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(Received April 14, 1939)

A comparison is made of the utility of the gas ion clustering hypothesis and of a free atom or free radical chain mechanism reactions taking place under ionizing conditions.

IN THE strictest sense ionization and excitation represent quite different states of the molecule. In both, an electron is displaced from its ordinary energy level. In the one case it is removed entirely from the molecule leaving a positive ion which may or may not be stable. In the other case, that of excitation, the electron is displaced to a higher energy level in the molecule which again may or may not lead to molecular dissociation.

Both normal and excited atoms, as well as free radicals, can result from either type of activation as a consequence of the primary steps of ionization or of excitation. It has long been a question, and one very difficult of solution, as to what if any intermediate processes occur between the primary step of ionization and the stabilization of the final chemical products. As in most problems of chemical kinetics, this evidence is for the most part indirect, often unsatisfactory, and inconclusive or contradictory.

While it has been easy to evolve theories that appear qualitatively plausible, it has proved much more difficult to substantiate them quantitatively.

One of the early hypotheses regarding chemical action associated with gaseous ionization was that the ions themselves enter directly into reaction with neutral molecules and that final chemical stabilization is the result of recombination in the gas phase of positive and negative ions that may or may not be the original ions produced. Or the negative charge may simply be a free electron. This simple hypothesis arose naturally from reactions produced by alpha-rays where the exact number of primary ions and of the number of molecules entering into reaction bore simple quantitative relations to each other. These relations remained constant regardless of such variables as temperature, intensity of radiation and relative or absolute concentration of the reactants.

The further fact that in many of the reactions induced by alpha-rays the number of molecules reacting exceeds by small definite factors the number of ion pairs produced, led to the assumption that the initial ions (usually the positive ions) may cluster neutral molecules about themselves before reacting at the time of neutralization and that at least some of those clustered molecules likewise react.

The phenomenon of ion clustering has long been known to physicists, but unfortunately the exact knowledge of it is very unsatisfactory. The positive ray method is usually applicable only at low pressures where collisions and clustering cannot take place. Attempts to bridge the gap by forming ions at higher gas pressure and then reducing the pressure rapidly to the positive ray range, have given evidence of clustering up to two to four molecules. But this is not nearly sufficient to explain cases where as many as 20 molecules react per ion pair, as in the case of the polymerization of acetylene under alpha-radiation. However, this failure to detect clustered ions of higher order cannot be interpreted as proving that they do not exist. For it is quite likely that such clusters are in a state of dynamic equilibrium dependent on collisions and pressure. Consequently as soon as the pressure is reduced they dissociate and are incapable of being detected by the positive ray method, whereas the reactions themselves are carried out only at relatively high pressures.

The method of ion mobility as far as it is applicable, has given some evidence which at least is not contradictory to the clustering hypothesis.

The above statements about reactions slightly in excess of ionization (2–20-fold) are not to be confused with chain reactions where the excess

* Presented at the symposium on "Kinetics of Homogeneous Gas Reactions." See page 725.

may reach a million-fold or even explosive reaction. The chain mechanism has been shown to be common to the same reactions when induced either by light quanta or by ions. What the steps are between the primary process and the chain mechanism is open to the same kind of questions as in the case of the nonchain reaction.

The cluster theory of the chemical action induced by ions was first proposed by Lind.[1] Its most successful application seems to have been in the cases of polymerization of unsaturated hydrocarbons. Beginning with the lowest members such as acetylene or ethylene, solid or liquid products of high molecular weight are readily obtained, which are direct proof of additive reaction. Whether this be by direct addition to a central ion before its neutralization or whether by a step-wise process initiated by an activated product of the ionization is the question about which a great deal of controversy has taken place.

The cluster hypothesis has been espoused and elaborated by Mund[2] and by Rideal,[3] for alpha-ray reactions and by Brewer and Westhaver[4] for reactions in glow discharge, and by Livingston[5] who has proposed a "hot molecule" theory involving utilization of the heat of neutralization to establish a dynamic equilibrium.

On the other hand, H. S. Taylor has advanced the idea that the gas ion reactions proceed through the intermediate step of free or excited atoms or free radicals. Eyring, Hirschfelder and Taylor[6] have succeeded in formulating the experimental data of Capron[7] for the conversion of para- to orthohydrogen by alpha-particles at room temperature. The reaction promoted by H atoms is a chain mechanism of 700–1000 length. Also in the alpha-ray oxidation of carbon monoxide by oxygen and of oxygen to ozone, Hirschfelder and Taylor[8] have obtained correlation by the mechanism of O atoms. Neither of these reactions is a chain reaction.

In the synthesis of HBr one meets a much more complicated case. The chemical yield per ion pair (M/N) instead of remaining constant, as in most cases, varies widely with temperature, with intensity of alpha-radiation, with the pressure and with the relative concentrations. Also the reverse reaction is pronounced. To meet this complicated situation Lind and Livingston[9] proposed a new type of cluster theory taking into account the factors referred to above, while Eyring, Hirschfelder and Taylor[10] attempted formulation based on the formation of hydrogen atoms as in the photochemical reaction. They were not able to obtain correlation without assuming the direction action of ions in one of the reaction steps.

One reaction which has not lent itself to successful treatment by any mechanism other than that of clustering about an ion is the polymerization of acetylene by alpha-rays. The yield is a definite one of about 20 molecules reacting per ion pair independent of temperature, concentration, and intensity of radiation. An additional piece of evidence of great significance is the behavior of mixtures of acetylene with the inert gases. While the latter do not themselves react under alpha-radiation, they cause acetylene to undergo polymerization at a rate enhanced by the additional amount of inert gas ions. In other words, if one is dealing with acetylene under such conditions of pressure that an alpha-particle can pass entirely across the reaction vessel and still lose a considerable portion of its energy to the wall of the containing reaction vessel, then the addition of an inert gas will absorb part of the energy and produce additional ions in proportion to the concentration and the stopping power of the inert gas. And most important for our present discussion is the fact that additional polymerization of acetylene is caused in exact proportion to the additional ionization whatever the inert gas be. This is a very striking and conclusive piece of evidence. The amount of xenon which must be added to a given amount of acetylene to double the ionization is only about

[1] S. C. Lind, Tr. Am. Electrochem. Soc. **44**, 63–75 (1923).
[2] W. Mund, Ann. Soc. Sci. Bruxelles **51**, 6 (1931); Bull. Soc. Chim. Belg. **36**, 19 (1927); **43**, 100 (1934); *L'Action chimique des rayons alpha* (Hermann et Cie., Paris, 1935).
[3] E. K. Rideal, Trois. conseil chim. Solvay, p. 1 (1928).
[4] A. K. Brewer and J. W. Westhaver, J. Phys. Chem., **34**, 162; 3254 (1930).
[5] R. S. Livingston, Bull. Soc. Chim. Belg. **45**, 334 (1936).
[6] Eyring, Hirschfelder and Taylor, J. Chem. Phys. **4**, 47 (1936).
[7] P. C. Capron, Ann. Soc. Sci. Bruxelles **55**, 222 (1935).
[8] J. O. Hirschfelder and H. S. Taylor, J. Chem. Phys. **6**, 783 (1938).
[9] S. C. Lind and R. Livingston, J. Am. Chem. Soc. **58**, 612 (1936).
[10] Eyring, Hirschfelder and Taylor, J. Chem. Phys., **4**, 570 (1936).

1/10 of that of the amount of helium which would be necessary to produce the same doubling in rate. It is therefore evident that ionization is the primary step involved in the alpha-ray polymerization of acetylene. The further fact that it is indifferent what ion induces the reaction, enhances the reliability of the cluster mechanism or makes other hypotheses so indirect that they appear improbable. The data[11] do not indicate that excited states play any role in the alpha-ray reaction, though it should be recalled that a similar product is obtained under ultraviolet radiation but with a quantum yield about one-half that of the ion yield.

Since the cases where hydrogen is one of the reactants in alpha-ray reactions have given promise of successful treatment on the basis of hydrogen atoms as the activated agent, two other reactions[12] are suggested for consideration, namely, the reduction of CO_2 by H_2 and of CO by H_2 using alpha-rays. It has been shown conclusively that the ionization of neither hydrogen alone nor of either CO_2 or CO alone, can explain the mechanism of the reactions. The sum of the ionizations of both hydrogen and of the respective oxide of carbon is necessary to give a satisfactory correlation. The consideration of hydrogen alone is quite out of the question. Of course exchange ionization might be considered, but whether H atoms would result from such an exchange is not experimentally known.

At present it seems fair to conclude that certain cases may be best treated on the hypothesis of free atoms, and indeed this has always been necessary in the case of the chain reaction between H_2 and Cl_2 induced by alpha-rays. In other cases, a cluster mechanism remains preferable, while in very complicated cases such as the alpha-ray synthesis of HBr it is necessary to combine both methods of attack even for the data at ordinary temperature. The known influence of temperature on the reaction introduces a further complication, but suitable data to undertake a solution are not yet at hand.

In the foregoing, scant attention has been paid to reactions brought about by electrical discharge in gases, though there is just as much reason to suppose that ions and free atoms will play the same roles as in the alpha-ray reactions. A similarity of products in the two types of reaction has been demonstrated,[13] but the opportunity to use these reactions to examine definite hypotheses is much less propitious than in the alpha-ray reactions, on account of lack of knowledge of the quantity of ionization and the inability to vary the reactants without introducing an unknown influence on the discharge conditions and consequent ionization.

[11] J. Am. Chem. Soc. **48**, 1575–85 (1926).
[12] J. Am. Chem. Soc. **47**, 2689; 2694 (1925).
[13] G. Glockler and S. C. Lind, *Electrochemistry of Gases and Other Dielectrics* (Wiley & Sons, New York, 1939).

Discussion

W. A. Noyes, Jr., *University of Rochester:* What are the ionization potentials of xenon and acetylene?

S. C. Lind, *University of Minnesota:* Xenon 10.06 and acetylene 12.0 volts.

W. A. Noyes, Jr., *University of Rochester:* An ionization potential of a molecule may involve displacement to one of the higher vibration states. Acetylene may seem to have a higher ionization potential than xenon but the energy may actually be lower. This might be an explanation of the fact that the addition of xenon increases the yield of polymerized acetylene.

Henry Eyring, *Princeton University:* An atom when ionized or even when excited becomes essentially a new element as far as its chemical behavior goes. Thus ionized xenon is a very reactive form of iodine. The enhanced activity comes from the positive charge added to what is essentially an iodine atom. This positive charge greatly enhances the reactivity of an iodine atom for addition to the triple bond in acetylene. When this bond has once been opened by addition of Xe^+ polymerization with other acetylene molecules proceeds in the normal fashion. The question naturally arises whether neutralization of the Xe^+ in such a lengthening polymer would stop its growth. Neutralization would cause the

xenon to be expelled but after a very few acetylenes have been added this cannot make much difference to the growing polymer. Thus there seems to be no reason why Xe^+ shouldn't be about as effective in promoting polymerization as acetylene ions or most any other kind of ions since all of them by ionization are changed into very reactive atoms or radicals in this same way. Beside the Xe^+ ions excited Xe^+, being likewise chemically active, should also add to the triple bond and start polymerization. Thus even if the electrons are not as effective in starting polymerization—apparently they are not readily absorbed by acetylene—it is not surprising that the polymerization yield per Xe^+ should be about twice that per absorbed quantum in photochemical polymerization.

S. C. Lind, *University of Minnesota:* I have no objection to that view. I forgot to mention one piece of new experimental evidence. We made an attempt to find the ion clusters with a mass spectrometer. Unfortunately it was necessary to produce the ions by bombardment with electrons instead of alpha-particles. We produced the ionization and used a system with six vacuum pumps to reduce the pressure at the end of the tube. We didn't find any more than a doubling of the molecular weight but I don't believe that this fact means that clusters cannot exist physically. If they are in a dynamic state of equilibrium, a cluster of 20 at one atmosphere's pressure may dissociate into double molecules at lower pressures.

O. K. Rice, *University of North Carolina:* Is there any evidence that the yield per ion pair falls off at extremely low pressures?

S. C. Lind, *University of Minnesota:* They do drop off at pressures of 1 to 2 mm. I am not sure that there is any relation between the dropping off and the theory of collisions since the dropping off in yield starts in at higher pressures than are calculated from the collision theory.

O. K. Rice, *University of North Carolina:* Perhaps this could be interpreted on the basis of the cluster theory. If the clusters are in equilibrium, a condition of saturation should exist at the higher pressures, in which the amount of clustering reaches a maximum. At sufficiently low pressures the gas would no longer be saturated with clusters and lower ion yields might be found.

Henry Eyring, *Princeton University:* Might you interpret as supporting the cluster ion theory the fact that the yield of chemical products per ion pair is about twice as large as the yield per quantum in photochemical experiments?

S. C. Lind, *University of Minnesota:* That has been suggested. Professor Mund believes that the cluster is like close-packed billiard balls and argues that the yield of 20 acetylene molecules per ion pair represents recombination before the complete close-packed ion is formed to a total of 26; 13 for the positive and 13 for the negative acetylene ion (if the latter exists).

D. C. Grahame, *University of California:* Have you ever noticed any anomalous results from the addition of carbon tetrachloride? Electrical discharge experiments show that traces of carbon tetrachloride inhibit ionization in the gases. Might not carbon tetrachloride have an inhibiting effect here similar to that of nitric oxide in ordinary chain reactions?

S. C. Lind, *University of Minnesota:* I don't believe that we have tried it. In the electrical discharge the carbon tetrachloride molecule tends to double. I should have said earlier that according to another explanation excitation is involved as well as ionization. When an alpha-particle passes too far away from a molecule to cause ionization, it may still excite the molecule. Rosenblum found that carbon dioxide is only about 14 percent efficient. The inert gases of this type are often inefficient.

J. O. Hirschfelder, *University of Wisconsin:* Professor Hugh S. Taylor and myself have interpreted the 14 percent efficiency of the CO_2 in the oxidation of CO as one of the strongest pieces of evidence against the ion cluster theory. In the mass spectrograph about one-fifth of the ions formed in CO_2 are CO^+ which, when neutralized, forms C+O. The C reacts with CO to form C_2O which is readily oxidized to CO_2 +CO. The O oxidizes another molecule of CO.

So altogether, for each five molecules of CO_2 ionized we expect one additional molecule of CO_2 formed and our expectations are in quantitative agreement with the experiments of Lind and Rosenblum.

S. C. Lind, *University of Minnesota:* With pure carbon dioxide there is no reaction at all. Unless one assumes that carbon monoxide is reoxidized immediately there seems to be a difficulty.

J. O. Hirschfelder, *University of Wisconsin:* When the concentration of O_2 becomes appreciable it will serve as a catalyst for the recombination of CO and O by the intermediate formation of ozone. The reactions involved are known to be fast. Thus an equilibrium state between CO_2 and $CO+O_2$ is reached after a small quantity of O_2 is formed in the reaction vessel.

Henry Eyring, *Princeton University:* Is there any difference in the ion yields between liquid and gaseous water?

S. C. Lind, *University of Minnesota:* The evidence is not strictly quantitative but data on hydrocarbons such as paraffin indicate that the reaction is the same in the liquid and gaseous states but a definite difference has been noted for water.

The Influence of Temperature and Pressure on the Infra-Red Absorption Spectrum of Gaseous and Liquid Hydrogen Chloride up to the Critical State*

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(Received May 24, 1939)

The absorption spectra, near 1.7μ, of liquid HCl from -100°C to the critical temperature of 52°C, and of gaseous HCl from one atmosphere to the critical pressure of 82 atmospheres, have been measured. The spectrum of the gas retains P and R branches about an origin undisplaced from its low pressure value up to just below the critical pressure, although discreet rotational lines are not recognizable after the density of 0.1 g/cc has been reached. At all temperatures, the transition of gas to liquid is accompanied by the replacement of the P–R branched type of spectrum by a single maximum displaced to low frequencies from the gas origin by an amount increasing from 48 to 117 cm^{-1} as the temperature is lowered from the critical temperature to -100°. This band is asymmetric, with a tail to the short wave side, and above 20°C shows signs of being resolved into two bands, one in the position of the gas band. It is concluded that liquid HCl contains two types of molecules, one gas-like, the other, with the vibration frequency perturbed by intermolecular action. The variation of the perturbed frequency with temperature is partly consistent with the hypothesis that the perturbation originates in the electrostatic action of neighboring molecules, but the magnitude of the shift is smaller by a constant amount than that produced by inert solvents of the same dielectric constant as liquid HCl. The gas a few degrees above the critical temperature and above the critical pressure also contains some liquid-like molecules.

IT has been shown[1] that liquid hydrogen chloride, bromide and iodide have absorption bands in the neighborhood of the 0−2 rotation-vibration bands of the corresponding gases which differ in several respects from the gas bands. Only a single absorption maximum was observed in the liquid, in contrast to the well-marked positive and negative branches of the gas band, the maximum was displaced to long wave-lengths from the gas origin, and the intensity relations in the liquid were markedly different from those in the gas; HI, for instance, showing in the liquid state a very great increase in absorption intensity compared with its quite feeble gaseous absorption. These results, observed with a double quartz prism instrument, were confirmed for HCl under the higher resolving power of a grating,[2] and meantime, Hettner had demonstrated corresponding differences in the nature of the absorption in the region of the 0−1 vibrational transition in gaseous and liquid HCl.[3] Recently, Vodar, Freymann and Yeou Ta have investigated the liquid and gas absorption of this substance in the region of the 0−3 vibrational band, at about 1.2μ, up to a temperature of 14°C, with similar results as to the form and position of the liquid band, and made the additional observations that the negative displacement of the liquid from the gas band decreased with the increasing temperature, and that there appeared in the low temperature liquid an additional broad weak band at longer wave-lengths than the main band, which disappeared with increasing temperature.[4]

The object of the experiments reported here was to study the nature of the changes in absorption accompanying the gas-liquid transition as the pressure of the gas was varied from atmospheric to the critical pressure of some 82 atmospheres and the temperature of the liquid was increased from about -100°C to the critical temperature of 52°C. In the gas the pressure range from 1 to 11 atmospheres has already been covered by the careful work of Becker,[5] who found a decided broadening of the rotational lines with increasing pressure, but no detectable displacement of their absorption maxima.

EXPERIMENTAL PROCEDURE

The instrument used was the grating spectrometer already described[2] which has a grating

* Read at the meeting of the American Chemical Society, Baltimore, April 3–7, 1939.

[1] E. O. Salant and W. West, Phys. Rev. **37**, 108 (1931).

[2] W. West and R. T. Edwards, J. Chem. Phys. **5**, 14 (1937). Dr. O. R. Wolf has drawn our attention to the fact that the frequency scales in the diagrams of the 0−2 bands in this paper are inverted, end for end. The frequencies as given in the tables and text are correct.

[3] G. Hettner, Zeits. f. Physik **89**, 234 (1934).

[4] B. Vodar, R. Freymann and Yeou Ta, J. de phys. et rad. VII. **9**, 282 (1938).

[5] G. Becker, Zeits. f. Physik **34**, 255 (1926).

with a ruled surface 5×4 inches of 3600 lines per inch, used in the region of the second order of 1.7μ. The desired pressures of HCl were realized by heating to the appropriate temperature a quantity of liquid HCl in a closed vessel, and the absorption determined by placing the saturated vapor in the light path furnished by a 500-watt incandescent filament projection lamp. An image of the filament was projected by means of glass lenses at the center of the absorption tube, which was mounted in a thermostat, and the emerging light collected and projected by a lens and mirror system on the entrance slit of the glass prism monochromator which supplied the grating instrument with light of the desired region.

The pressure cell is shown in Fig. 1. The material was the copper-silicon-manganese alloy Everdure, which combines high tensile strength with high chemical resistance to gaseous and liquid HCl. The length of the absorbing layer could be altered by the addition or removal of spacers *C*. Glass windows were used, 20 mm thick and 25 mm clear aperture, held in the metal pieces *A*, by means of thoroughly polymerized Bakelite cement BC-6035, B92. This cement proved completely resistant to attack by liquid and gaseous HCl under the most extreme conditions of temperature used, and was the only cement of the many tried which combined inertness with the ability to form a pressure-tight seal.* The cell was kept tight by forcing the pieces *A* against the lead washers *D* by means of the screws *E*. Adequately dry liquid or gaseous HCl was found to produce very little corrosion of the washers under any of the conditions used here.

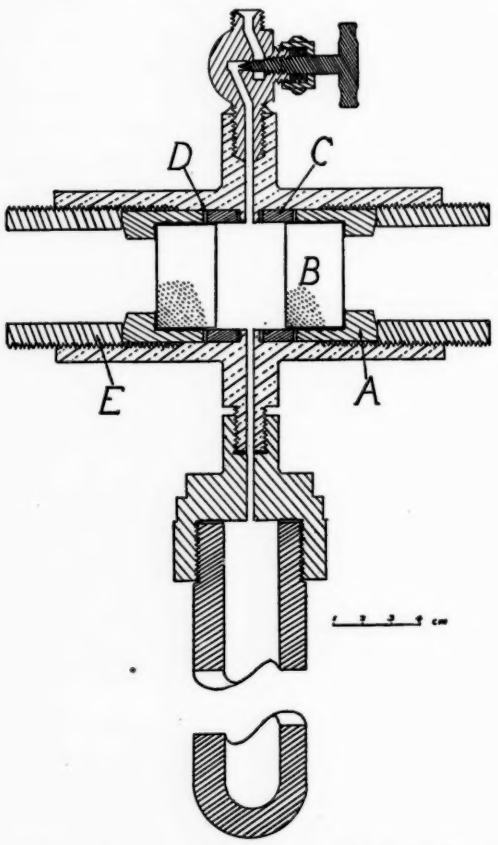

FIG. 1. Absorption cell of adjustable thickness for gases and liquids under pressure.

To fill the cell, the lower reservoir was unscrewed from the absorption chamber, closed with a rubber stopper provided with inlet and outlet tubes, and attached to a generating train. HCl was produced by dropping concentrated sulphuric acid on hydrochloric acid solution, dried by bubbling through sulphuric acid and over phosphorus pentoxide, and liquified in a glass reservoir by cooling in liquid air. The middle third of the liquid was then condensed in the pressure reservoir, the level of the liquid in the metal tube being indicated by a glass float and pointer arrangement projecting into the glass outlet tube. On the outside of this was pasted a scale calibrated in terms of the amount of liquid in the metal reservoir. After the collection of the necessary quantity of liquid, the rubber stopper was removed and the absorption cell quickly screwed home. This operation was the weak point in the filling, owing to the possibility of the introduction of moisture, but days of low humidity were chosen for filling, and usually, the condition of the lead washers on reopening after a run or series of runs showed that insig-

* Some difficulty was experienced in making a tight seal with Bakelite cement. The trouble lies in the evolution of bubbles, presumably of steam, during the last stages of the polymerization, which tend to form runnels. If the glass and metal parts to be joined are separately coated with a thin layer of the cement, from which much of the solvent has been removed by careful heating, and these layers polymerized separately at as low a temperature as possible (say by heating overnight at 110°) and if now the window is sealed in the metal part by an additional thin layer of cement which is slowly polymerized by heat, a pressure-tight and exceedingly strong seal is produced capable of standing temperatures of at least 100°C under pressure.

nificant quantities of water vapor entered the cell during the attachment of the absorption chamber.

In experiments above room temperature the cell was placed in an air thermostat provided with a heating coil, fan and conventional mercury regulator. Temperatures were read by means of a copper-constantan couple in contact with the outside of the absorption chamber. In the low temperature experiments ice was prevented from condensing on the cell windows by placing over the ends of the absorption chamber Bakelite tubes projecting out from the thermostat and closed with glass windows. The air inside the tubes was dried by calcium chloride, and the low thermal conductivity of Bakelite usually prevented the outer windows from being cooled to the dew point of the air in the room; on humid days a small heating coil kept these windows sufficiently warm. The low temperature thermostat consisted of two rectangular parallelepipedal tin cans, one within the other, with ends removable for the introduction of the cell. A space about an inch wide separating the cans could be filled with dry ice, the whole being placed in a box of Celotex. A heating coil and bimetallic regulator allowed the adjustment and maintenance to 0.1° of any temperature desired above that of dry ice, the cold air being well stirred by a fan mounted on a hard rubber axle passing through the walls of the thermostat.

The same cell served both for liquid and gas: to investigate the liquid, the cell was turned reservoir up so that the liquid ran into the absorption chamber.

Energy readings with the empty cell necessary for the computation of percentage transmissions were obtained by placing the cell in the thermostat and freezing the HCl by liquid air. Not later than one day after a measurement, the calibration of the instrument was checked against several lines of the HCl gas absorption at one atmosphere: Meyer and Levin's[6] values for the major component of the isotopic doublets were taken as standards.

Results

The general nature of the results in indicated by the transmission-wave-length curves of Fig. 2. The left side horizontal portion of each curve represents complete transmission, and the scale of ordinates, which is the same for all curves, is indicated by the completely drawn scale for the lowest curve. The thickness of the absorbing layers for the various curves are, from the topmost down, 100 cm, 1 cm, and for all the others, 0.4 cm. The curves for the liquid absorption at $-100°$ and $-77°$C are not reproduced, but are of the same form as that at $-43°$, with a displacement of the maximum of absorption towards lower frequencies. The pressures recorded in these curves are the values of these quantities for the saturated vapor at the experimental temperatures, as obtained from Landolt-Börnstein.[7]

In describing the effect of increasing pressure on the gas absorption, we recall the result of Becker already alluded to,[5] that the rotational structure persists, with much broadening of the lines, but without sensible displacement of their maxima, up to pressures of some 11 atmospheres. It will be seen, from Fig. 2 that even at 21 atmospheres, the individual lines of the negative branch, whose separation is greater than that of the positive lines, are still resolvable,

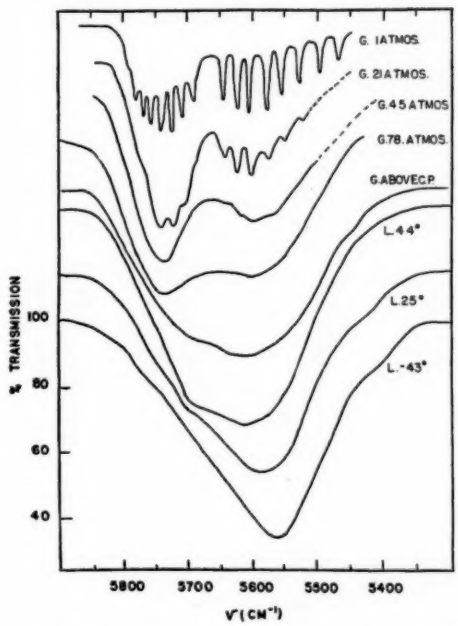

FIG. 2. Absorption of gaseous and liquid HCl at different temperatures and pressures.

[6] C. F. Meyer and A. A. Levin, Phys. Rev. **34**, 44 (1929).

[7] Landolt-Börnstein, *Physikalisch-chemische Tabellen*, II, p. 1343.

without displacement of the maxima, and that a suggestion of the positive lines remains. At 45 atmospheres, the rotational lines have almost completely disappeared, and the absorption curve resembles the doublet predicted by classical theory for the rotation-vibration spectrum of a diatomic molecule. The minimum between the P and R branches is at the position of the "missing line" in the low pressure absorption, the feeble maxima are, in the P branch, within experimental error, at the position of the second, third and fourth lines of the low pressure gas, and the R maximum is between the third and fourth lines in that branch. At 78 atmospheres, corresponding to a few degrees below the critical temperature, all vestige of discreet structure has disappeared, but the classical doublet can still be discerned, with the minimum and two maxima in the positions required if the molecules at that pressure have the same vibration frequency and moment of inertia as at low pressures. The slight shift in the maximum of the R branch towards higher frequencies at high pressures as compared with at lower pressures is completely accounted for by the effect of the necessary temperature increase on the distribution of the molecules among the rotational states.

The form of the absorption curve in the liquid, and its temperature variation can be quickly described. Under no condition does the band resemble a rotation-vibration doublet. Up to about 20°C the band consists of a single rather sharp maximum, strongly asymmetric, with a tail towards the high frequencies; the maximum is displaced to low frequencies from the gas origin, the more displacement the lower the temperature. Above 20° the asymmetry becomes less pronounced and the maximum broader, and there appears in the absorption curve a point of inflection near the position of the gas minimum, as if the gas band might be present. The fourth curve from the bottom was obtained with the HCl a few degrees above the critical temperature: the critical phenomena (disappearance of the surface of small gas bubbles which had been rising through the liquid just below the critical state, and the critical opalescence) were observed both before the commencement of the measurements, and on cooling after their completion. The band here is essentially that characteristic of the liquid, as would be expected, since the only difference between the gas just above the critical condition and the liquid just below it, is that release of the pressure in the gas is accompanied by expansion, while the liquid has a surface. It may be relevant, in connection with the persistence, observed by Maass and his collaborators,[8] for some degrees above the critical temperature, of density differences in the material in the lower and upper portions of a vessel containing a liquid which has been caused to pass through the critical state, to remark that in this experiment the absorption spectrum was observed of material which had been liquid before the critical transition.

TABLE I. *Absorption maximum of 0–2 l.* HCl *band at different temperatures.*

T°C	−100	−72	−44	−13	25	35	48	55
d (g/cc)*	1.23	1.156	1.075	0.972	0.802	0.730	0.620	0.44
ν (cm^{-1})	5551	5561	5565	5571	5590	5602	5621	5620
$\frac{\Delta\nu}{\nu_0}\times 10^2$	2.06	1.89	1.82	1.71	1.38	1.16	0.83	0.83

* Interpolated from data in *Gmelin's Handbuch der Anorgan. Chem.* System-nommer 6, p. 114.

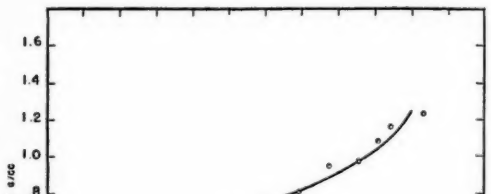

FIG. 3. Relative shift of liquid frequency as function of density (not at constant temperature).

Table I gives some details of the position of the liquid maximum at different conditions, and the way in which the relative displacement of the liquid band from the gas origin depends on the density is shown in Fig. 3. Extrapolation of the density-displacement curve indicates zero shift of the liquid band at a density of about 0.4 g/cc, near the critical density (0.424).

[8] O. Maass and A. L. Geddes, Phil. Trans. Roy. Soc. **A236**, 303 (1937).

The whole situation with respect to the variation with density of the infra-red spectrum of HCl in the region here considered seems then to be summed up as follows. There is no essential change in vibrational frequency or moment of inertia of HCl molecules with increasing density up to density of about 0.26 g/cc (pressure = 78 atmos.). Somewhere between this value and the critical density of 0.424 a change in character of the absorption occurs from that characteristic of the gas to that characteristic of the liquid, a single maximum displaced to low frequencies from the gas origin, although approaching the critical state, there are signs that the liquid contains gas-like molecules. In the liquid the displacement from the gas origin increases with increasing density and decreasing temperature, at a diminishing rate the higher the density and the lower the temperature, and the absorption maximum becomes sharper.

In reporting a vibration frequency of the gas which is independent of density up to near the critical condition, we do not imply, of course, that small pressure shifts, of the order of those observed in atomic lines may not take place. At high pressures the minimum in the gas absorption which we associate with the band origin is very flat, and its position is uncertain to about $\pm 5\ \mathrm{cm}^{-1}$; the maximum of the P branch can be accurately ascertained, and as its position coincides within $2\ \mathrm{cm}^{-1}$ with that to be expected if the vibrational frequency retains its low pressure value, it seems true to state that within these limits there is no change on the vibrational frequency in the gas up to a pressure of 78 atmospheres.

Discussion

Three separate effects are involved in the changes from gas-like to liquid-like absorption in HCl: (1) the replacement of the rotationally-quantized gas spectrum by the classical rotation-vibration doublet at densities of about 0.1 g per cc; (2) the replacement, at densities between 0.26 and 0.45, of the gas type of absorption by the liquid type; and (3), the shift of the liquid maximum to lower frequencies with diminishing temperature and increasing density of the liquid.

The first problem can be easily dismissed, in at least a phenomenological way. Whatever may be the details of the effect of the interaction of the neighboring molecules on the rotational levels, it is evident that at these densities the frequency of collisions becomes comparable to the period of a single rotation, and as the probability of a change in rotational state on collision is high, the time of a molecule's existence in a given state is small, bringing about as a result of the uncertainty relation $\Delta E \times \Delta t \doteqdot h$, a broadening of the energy levels. The distribution of energy among the rotating molecules is unaltered by the increase in density, with the result that a minimum of absorption occurs in the region corresponding to low rotational states, and two branches can be recognized, which can be interpreted as P and R branches in the ordinary sense. Owing to the smaller interval between the lines in the R branch, the overlapping here is more pronounced than in the P, and the intensity of the R branch appears greater than that of the P, apart from the theoretically greater intensity of the R branch even at low densities.

The change in the character of the absorption from the gas-like to the liquid-like involves a more fundamental perturbation of the HCl molecules than that just discussed. If an increase in density beyond the critical density merely further increased the broadening of the rotational levels, an absorption with a single maximum might eventually be observed, but it would be unsymmetrical in the sense of concentrating the absorption on the high frequency side, instead of in the opposite sense as is observed. It seems much more in accord with the observations to conclude that in the liquid a new band appears, constituted of a single maximum, displaced towards the low frequencies from the gas origin. The maximum will then represent the most probable vibration frequency of the perturbed molecules in the liquid. The asymmetry of the band suggests that there may also be present another overlapping band with a center near the gas origin, to be attributed to gas-like molecules in the liquid, whose state is much the same as that of molecules in the gas at high pressure. Above about 20°C, indeed, the two bands seem to begin to be separated. It is possible to reproduce the observed shapes of the

liquid band at different temperatures by the superposition, in different relative amounts, of two symmetrical bands, one with a maximum at the value of the gas origin, the other with its maximum displaced some 50 to 100 cm^{-1} to the lower frequencies, according to temperature. On this interpretation, and on the assumption that the molar absorption coefficients are the same for both bands, the fraction of "liquid molecules" in the liquid at 20°C is about 0.2, while at −100° it is 0.9.

The conclusion we are led to by these considerations is therefore of the existence in the liquid, in various proportions determined by the temperature, of two rather sharply contrasted types of HCl molecules, some in a state of relatively low perturbation, and possessing an internuclear vibration frequency and internuclear distance nearly the same as isolated molecules, and others, subject to greater intermolecular forces, the characteristic "liquid" molecules, whose internuclear frequency is lowered and presumably whose internuclear distance is increased, from the values in the gas.

As to the nature of the perturbations in the liquid, it seems impossible to evade the thermodynamic evidence against any great amount of dimeric or polymeric association in HCl involving the formation of linkages of greater strength than are found in "normal" liquids. The Trouton constant has nearly the value for a normal liquid, and the data on vapor pressure as a function of temperature, treated according to Hildebrand's rule,[9] give the completely normal value of 13.8 for L/RT_c. In this connection it is relevant to discuss the results of Vodar, Freymann and Yeou Ta[4] on the absorption of liquid HCl in the neighborhood of the 0−3 vibrational band. In addition to the main band, which is found to have the same characteristics of asymmetric shape and shift of the maximum towards low frequencies as the band described here, these investigators find, at low temperature (−80°C) a broad shallow band, with its maximum displaced about −380 cm^{-1} from the main band, which disappears as the temperature rises, This they attribute to "associated" molecules and the main band to "free" molecules. A corresponding band would be expected to appear at low temperatures on the low frequency side of the 0−1 and 0−2 bands, at about 4 and 1.9μ, respectively. The measurements of this paper extend only to 1.86μ, but no sign of the beginning of a new band is observed in the thickness used here (4 mm at −77°C) nor in the older measurements of Salant and West[1] out to 2μ in a thickness of 1 mm. These long wave bands, if they exist, near the fundamental and first overtone, are evidently more feeble, compared with the main band, than near the second overtone. This seems quite possible; differences in the values of the anharmonic constants of the vibration associated with the main band and its long wave companion could make the rate of diminution of intensity with increase in the vibrational quantum number of the excited state less for the satelite than for the main band, so that a thickness of absorbing layer which gives a convenient absorption in the main band would show the other relatively more intense than in the regions corresponding to lower vibrational transitions. Appearances of this nature are observed, for instance, in the principal bands and satelites in dissolved HCl. Be this as it may, it is evident that any association in HCl involving the existence of stronger intermolecular binding than in normal liquids is, at most, limited to low temperatures, and is of small amount.

Having dismissed an interpretation of the liquid band in terms of polymerization, we proceed to discuss to what extent the situation in liquid HCl is illuminated by the theory advanced by Kirkwood,[2] and more recently by Bauer and Magat,[10] which gives an expression for the change in frequency experienced by a dipole on its immersion in a dielectric medium as a result of electrostatic interaction between dipole and medium. This theory has proved qualitatively adequate to account for the absorption of HCl dissolved in certain solvents,[2] which exhibits resemblances to that of liquid HCl in that the chief feature is a strong maximum, displaced towards low frequencies from the gas origin, though it should be mentioned that a marked difference is the appearance of subsidiary maxima on both sides of the main band. Kirk-

[9] J. H. Hildebrand, J. Am. Chem. Soc. **37**, 974 (1915).

[10] E. Bauer and M. Magat, J. de phys. et rad. VII, 9 (1938).

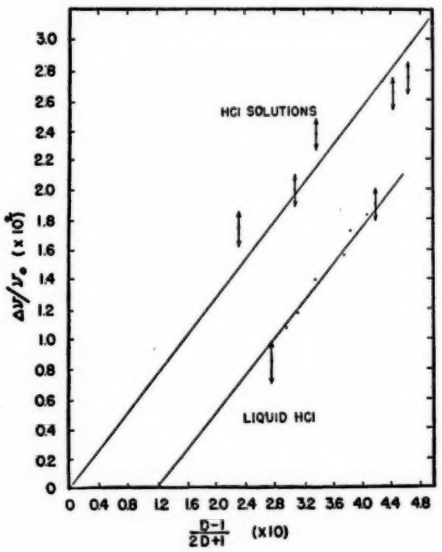

FIG. 4.

wood's relation for the relative shift of the perturbed band from the gas origin, $-\Delta\nu/\nu_0 = C(D-1/2D+1)$, where D is the dielectric constant of the medium and C a quantity containing the electric moment of the oscillating dipole and its first and second distance derivatives and certain size factors, was shown to yield the correct order of magnitude for the frequency shift accompanying the gas-solution and the gas-liquid transition at low temperature, and to account for, at least qualitatively, the dependence of the shift on the nature of the solvent in solutions in chemically inert solvents. It is then of interest to see to what extent the change of the liquid maximum with temperature can be interpreted as due to changes of the dielectric constant of liquid HCl with temperature. If the molecular constants in the expression for the shift are independent of temperature and density, the relative shift is linear in $D-1/2D+1$. Fig. 4, in which $\Delta\nu/\nu_0$ is plotted against this expression (the values of D being interpolated from the measurements of Glockler and Peck,[11] shows that within the precision of the measurements of the shifts, indicated by arrows drawn from the experimental points, a straight line passing through the origin does describe the trend of the solution shifts[2] with dielectric constant, but that the liquid points lie on an approximately parallel line which does not pass through the origin. The way in which the shift varies with temperature and density of the liquid, and its general magnitude, are compatible with the theory that it is due to the electrostatic interaction of neighboring molecules, but it would seem that some constant subtractive factor is at work which makes the value of the shift in the liquid smaller than in inert solvents of the same dielectric constant.

[11] G. Glockler and R. E. Peck, J. Chem. Phys. **4**, 658 (1936).

Vibration Spectra and Molecular Structure

VIII. Absorption Spectra of Light and Heavy Phenol and Aniline Vapors*

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(Received May 19, 1939)

The near infra-red spectra of light and heavy phenol and aniline vapors have been obtained with a rocksalt spectrometer. Comparisons have been made between the spectra of the light compounds as found in various phases, and an interpretation of certain changes occurring in the spectrum of phenol is suggested. The spectra of the heavy compounds have suggested certain assignments, such as the δ (OD) vibration at 913 cm^{-1} in heavy phenol and the δ (OH) vibration at 1177 cm^{-1} in light phenol.

INTRODUCTION

FOR some time the authors have been interested in investigating the absorption spectra of the vapors of compounds in order to study the properties of individual molecules. By studying vapors one eliminates the effects of neighboring molecules which are present in solids, liquids, and at times in solutions. It seemed nteresting to investigate some simple aromatic compounds in the vapor phase which had been examined previously in other phases in order to make a comparison between the spectra obtained in these various ways. Two of the simpler aromatic compounds are phenol and aniline, both of which can be deuterated readily. From a comparison of the spectra of a light and a heavy compound one should expect considerably more information than from the light compound alone. Since phenol has been studied by various authors in the solid and liquid phases and in solution,[1–4] we had at our disposal the necessary information to attempt these comparisons. Unfortunately, aniline has not been studied so thoroughly as phenol.[3, 5]

We also hoped to assign bands to characteristic modes of vibration in these molecules. Many investigators have apparently assumed in making their assignments that the liquid or solid spectrum can be taken as that of the single molecule. In certain instances this is a valid procedure because interactions are negligible, although in other cases this is certainly untrue. For instance, the liquid and vapor spectra of water[6] are quite different. This is also true for formic acid.[7] In contrast to formic acid, the liquid spectra of CH_3COOD, CD_3COOD, and C_2H_5COOD[8] are essentially those of the dimer vapors although, here too, there are many small shifts in the positions of bands. Frequently differences arise because hydrogen bonding is present in the liquid but not in the vapor phase, e.g., water and phenol, as this investigation shows. On the other hand, Buswell, Rodebush and Roy[9] have shown that the spectrum of acetic acid in CCl_4 solution and acetic acid vapor are practically the same in the high frequency region. However, Davies and Sutherland,[10] working with a band in this same region, claim that solvent effects must be taken into consideration before a heat of association of carboxylic acids, run in CCl_4 solution, can be found. Numerous investigations in recent years have shown that the positions of some bands depend on the solvent employed. It seems to us that further work, employing higher resolution, is desirable in order to clear up many of these problems.

* For a preliminary account of this work see Phys. Rev. **55**, 684 (1939).
[1] A. Naherniac, Ann. de phys. **7**, 529 (1937).
[2] J. J. Fox and A. E. Martin, Proc. Roy. Soc. London **A162**, 419 (1937).
[3] J. Lecomte, J. de phys. et rad. **8**, 489 (1938).
[4] R. R. Brattain, J. Chem. Phys. **6**, 298 (1938).
[5] Unpublished curves of R. R. Brattain.
[6] E. K. Plyler and C. J. Craven, J. Chem. Phys. **2**, 303 (1934); W. W. Sleator and E. R. Phelps, Astrophys. J. **62**, 28 (1925); B. Stansfeld, Zeits. f. Physik **74**, 460 (1932); J. R. Collins, Phys. Rev. **55**, 470 (1939).
[7] Unpublished data of L. G. Bonner and R. Hofstadter.
[8] Work done in this laboratory by P. Marzoni for senior thesis.
[9] A. M. Buswell, W. H. Rodebush and M. F. Roy, J. Am. Chem. Soc. **60**, 2239 (1938).
[10] M. M. Davies and G. B. B. M. Sutherland, J. Chem. Phys. **6**, 755, 767 (1938).

Experimental.

The experimental technique employed was essentially the same as that in previous investigations in this laboratory. In the present study it was necessary to heat the solid or liquid samples in order to obtain pressures high enough to give sufficient absorption. The samples were heated in a side tube brought out from the absorption cell in the main furnace. The side tube was wrapped with an auxiliary furnace whose temperature, measured by two thermocouples, controlled the vapor pressure in the main cell. The temperature in the main furnace was always kept higher than that in the auxiliary furnace in order to prevent condensation on the windows of the absorption cell.

The phenol and aniline employed were Kahlbaum products. Heavy phenol (C_6H_5OD) and heavy aniline ($C_6H_5ND_2$) were prepared by exchanging the light compounds with 99.6 percent heavy water several times. All these compounds were dried by heating in vacuum and were purified by distillation. Sodium was substituted for the hydrogen or deuterium of the hydroxyl radical of the heavy phenol, and the resulting H_2-D_2 mixture was analyzed in a mass spectrograph. The D/H ratio in the gas mixture was 12.1. However, because of the presence of impurities during the reaction, the D/H ratio in the hydroxyl radical may have been somewhat greater. Although the D/H ratio in the amino group was not determined for $C_6H_5ND_2$, the infra-red spectrum indicates that there is less than ten percent of hydrogen present in the amino group. Both the light and heavy compounds were distilled into the side tube of a cell previously baked out under vacuum for several hours at about 150°C.

To check the results shown in the curves and tables, we studied parts of the spectra at different pressures and temperatures; while in one case, (C_6H_5OH), the complete spectrum was taken at a different temperature (162°C) but at the same pressure as that shown in Fig. 1. Higher pressures, of course, produced deeper and broader bands, and some of the measured band positions were obtained under these conditions. However, under none of these varied conditions for a single compound was there any shift in band position outside the limit of error.

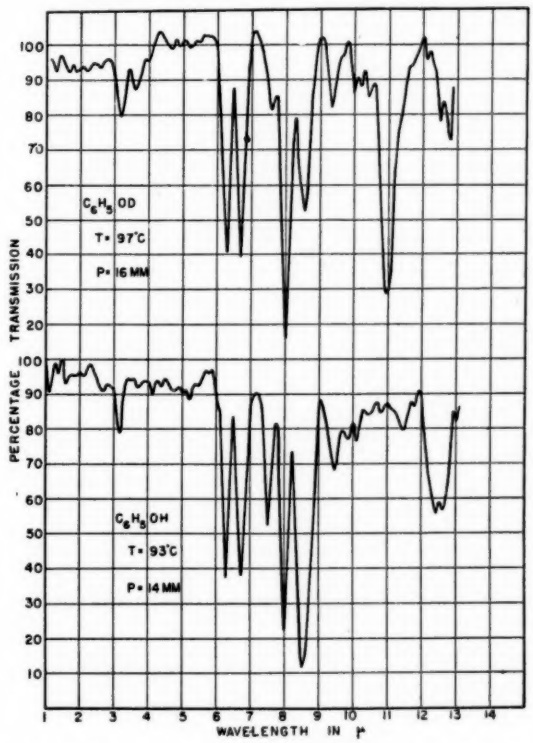

Fig. 1. Spectra of C_6H_5OH and C_6H_5OD vapors. Cell length 22 cm.

Results and Discussion

Phenol—OH and OD comparison

We have given our results on light and heavy phenol and aniline in Figs. 1 and 2 and Tables I and II. We may compare the spectra of C_6H_5OH and C_6H_5OD to help us draw conclusions regarding the assignment of bands. If we do this, we find that in C_6H_5OD two rather clear shifts to longer wave-lengths occur, namely, 2.7–3.65μ, and 8.5–10.95μ. We have assumed in recognizing this latter shift that the band near 8.5μ in C_6H_5OH is really (at least) double and that in C_6H_5OD only one of the bands remains. The shifted band has been assigned as a δ(OH) vibration. The same interpretation of a band near 8.5μ has been found to be satisfactory in a series of acetic acids recently studied.[11] The band at 10.95μ in C_6H_5OD is, therefore, the

[11] R. C. Herman and R. Hofstadter, J. Chem. Phys. **6**, 534 (1938).

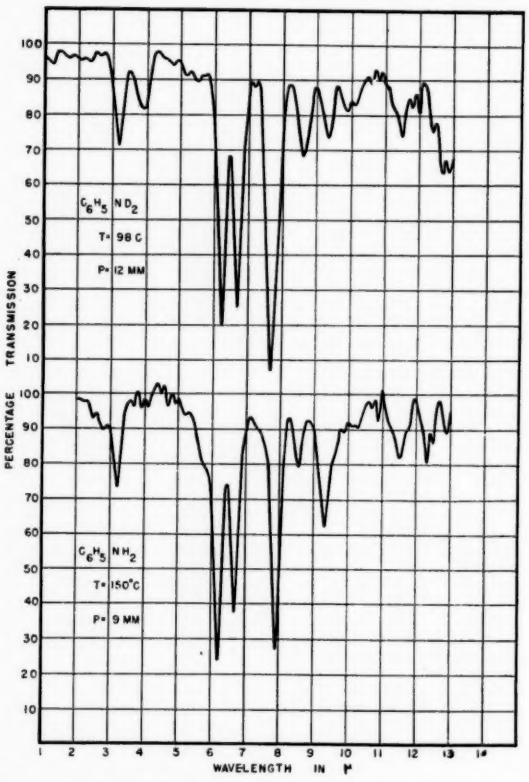

FIG. 2. Spectra of $C_6H_5NH_2$ and $C_6H_5ND_2$ vapors. Cell length 22 cm.

δ(OD) vibration. The one remaining near 8.6μ appears to be a δ(CH) vibration, probably ν_{9a}.[12] The first shift mentioned above is also connected with the hydroxyl group and the two bands are the OH and OD valence vibrations. Several common "benzene bands" appear in both C_6H_5OH and C_6H_5OD. These are the ones at 3.2, 6.3, 6.7, and perhaps 9.4μ. We have listed our interpretations of these bands in the tables. Since, in both the phenols, we could not find consistent interpretations for the bands at 7.5 and 8.0μ as modes of mono-substituted benzene, we have tentatively assigned these to the COH(COD) group.

Aniline—NH_2 and ND_2 comparison

We have found but one shift which can be clearly interpreted in the comparison of the $C_6H_5NH_2$ and $C_6H_5ND_2$ curves. This is the one from 2.8μ in the light aniline to 3.95μ in the heavy aniline. These bands are to be connected with the valence vibrations of the NH_2 and ND_2 groups, respectively. The other noticeable shift is that of a band moving to higher frequency in the heavy compound, namely, the shift 7.9–7.65μ. If these bands may be attributed to essentially the same mode in both molecules, the direction of the shift does not seem to be explainable. However, we have no other interpretation to give.

[12] A. Langseth and R. C. Lord, Jr., Det. Kgl. Danske Videnskabernes Selskab. Mathematisk-fysiske Meddelelser **16**, 6 (1938).

Spectra in different phases

On comparing our results on light phenol vapor with those on the liquid and solid obtained by R. R. Brattain[4] with the same instrument, we see that there are definite differences. We believe that most of the differences in this case can be correlated with the disappearance of hydrogen-bonding in the solid-liquid-vapor transition. The most striking difference is that in the vapor spectrum there is no broad association band in the region of 3μ in constrast to the spectra in the solid and liquid where it appears at 3.1 and 2.9μ, respectively. The shift in going from solid to liquid is probably due to the presence of differently associated forms in these two phases. The absence of the association band in the vapor spectrum agrees with the work of Fox and Martin on phenol in CCl_4 solution[2] and permits us to see the free ν(OH) vibration at 2.70μ and the ν(CH) at 3.20μ. The two bands appearing between 6 and 7μ show slightly different positions from the solid and liquid

TABLE I.

C_6H_5OH			C_6H_5OD		
$\lambda(\mu)$	(CM^{-1})	PROBABLE ASSIGNMENT	$\lambda(\mu)$	(CM^{-1})	PROBABLE ASSIGNMENT
2.70	3704	ν (O–H)	3.20	3125	ν (C–H)
3.20	3125	ν (C–H)	3.64	2827	ν (O–D)
4.08 *w*	2450		4.00 *w*	2500	
5.20 *w*	1922		5.20 *w*	1922	
5.70 *w*	1753		5.50 *w*	1819	
5.90 *w*	1695		6.29	1590	ν_{8a}, *b*
6.29	1590	ν_{8a}, *b*	6.70	1493	ν_{19a}
6.73	1487	ν_{19a}	7.60	1317	
7.52	1329		8.00	1250	
8.00	1250		8.58	1164	ν_{9a}
8.50	1177*	δ (O–H) and ν_{9a}	9.35	1070	
9.46	1057		10.00 *w*	1000	
9.90 *w*	1010		10.20 *w*	980	
11.41	876		10.40 *w*	962	
12.50	800		10.96	913	δ (O–D)
			12.50	800	
			12.80	782	

w weak.
* Probably at least double.

spectra. Brattain has shown that the band at 7.35μ in solid phenol shifts to 7.4μ in liquid phenol at 42°C, and then to 7.45μ at 101°C. We find the culmination of this process in the final appearance of this band at 7.52μ in the vapor at 93°C. There is no further shift with increasing temperature. This behavior indicates the close connection of this band with the COH group which is that part of the molecule directly involved in association phenomena. This confirms the entirely independent suggestion made earlier concerning the nature of this band.

From our results it becomes possible to attempt an explanation of the behavior of the bands in the region of 8.5μ.[13] In the solid spectrum we start with two bands at 8.15 and 8.7μ, respectively. In the liquid at 42°C, however, there is a single band at 8.25 which has an asymmetry near 8.75μ and at 101°C the band center is at 8.33μ. We suggest that, as the temperature is raised, more and more vapor-like molecules are formed whose characteristic bands near 8.5μ gradually deepen so as to cause the broadening and shifting toward 8.5μ that is observed. The fact that the 8.33μ band (at 101°C) is so broad would suggest that some of the solid-like molecules, with bands at 8.15 and 8.7μ, are still present to some extent. If we assign the strong band at 8.2μ to the associated δ(OH) vibration and, as previously noted, the 8.5μ band to the free δ(OH) vibration, then the shift from solid to vapor is toward lower frequencies as opposed to the valence vibration near 3μ which shifts to higher frequencies. This result has been found theoretically by Bauer and Magat.[14]

In the case of aniline, it seems to be true that though the vapor and liquid spectrum differences are less striking than in phenol, at least one may be explained as due to hydrogen bonding in the liquid.[5] Thus, the large band in the liquid at 2.9μ is to be ascribed to a hydrogen bond between nitrogens of neighboring molecules. Its replacement by "free" NH and ND bands in the vapor shows that the molecules are single.

TABLE II.

$C_6H_5NH_2$			$C_6H_5ND_2$		
$\lambda(\mu)$	(cm^{-1})	PROBABLE ASSIGNMENT	$\lambda(\mu)$	(cm^{-1})	PROBABLE ASSIGNMENT
2.80	3573	ν (N−H)	3.20	3125	ν (C−H)
3.21	3117	ν (C−H)	3.95	2532	ν (N−D)
5.20 *w*	1922		4.75 *w*	2107	
6.21	1612	$\nu_{8a,b}$	5.20 *w*	1922	
6.69	1594	ν_{19a}	5.55 *w*	1802	
7.92	1263		6.23	1606	$\nu_{8a,b}$
8.57	1168	ν_{9a}	6.69	1594	ν_{19a}
9.32	1074		7.67	1305	
11.50	870		8.60	1162	ν_{9a}
12.30	813		9.34	1071	
12.50	800		9.88	1012	
			10.10	990	
			11.50	870	
			12.40	807	
			12.80	782	

w weak.

[13] R. Freymann, J. de phys. et rad. **9**, 517 (1938). From his work on alcohols Freymann has offered a partial explanation of this behavior observed by Brattain and has suggested that the shifts are due to the absence of hydrogen bonding in the vapor.

ACKNOWLEDGMENTS

We wish to thank Mr. W. Guyer for his kind cooperation in analyzing our H_2-D_2 sample, and take pleasure in expressing our appreciation to the Research Department of the Calco Chemical Company for the interest they have taken in this work.

[14] E. Bauer and M. Magat, J. de phys. et rad. **9**, 319 (1938).

Thermodynamic Properties of Hydrogen Fluoride and Fluorine from Spectroscopic Data*

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Spectroscopic data have been used to calculate the free energy, entropy and heat capacity of diatomic HF between 298.1° and 2000°K. The required spectrum of F_2 is not known but from electron diffraction data and Badger's rule, enough information has been obtained to make similar calculations to the harmonic oscillator—rigid rotator approximation. The errors in the thermodynamic quantities due to the uncertainties in the vibrational frequency and moment of inertia have been estimated. Combination of these results with thermal data has resulted in values of the free energy change of the reactions: $1/2H_2+1/2F_2 \rightleftharpoons HF$ and $F_2 \rightleftharpoons 2F$.

BECAUSE of experimental difficulties, there is little available information on the free energy and other thermodynamic properties of hydrogen fluoride and fluorine gases. The spectrum of HF, however, is well known and reasonable estimates may be made for F_2, so that the free energy, entropy and heat capacity may be calculated from spectroscopic data with considerable confidence.

The rotation-vibration spectrum of diatomic HF has been studied by Imes,[1] by Schaefer and Thomas[2] and by Kirkpatrick and Salant.[3] From the three known bands, the latter have obtained several different values for the vibrational constants of the molecule. They have also found that the quantity, β_e which measures the variation of D_e with vibrational quantum number, changes sign in going from the $(1 \leftarrow 0)$ to the $(3 \leftarrow 0)$ band. The uncertainty of 18 cm^{-1} in ω_e, however, causes an uncertainty in the molar free energy, entropy and heat capacity at 2000°K of 0.0014, 0.0004 and 0.006 cal., respectively. These errors are unimportant for our purpose and the uncertainties in $x_e\omega_e$ and β_e are even less important. We therefore take the molecular constants determined by Kirkpatrick and Salant from all three vibrational bands, with $\beta_e=0$. The resulting values are given in Table I.

The free energy, entropy and heat capacity were calculated by well-known methods and are shown in Table II. The sum over states was obtained by interpolation in the tables of Gordon and Barnes.[4] The atomic weights of H and F have been taken as 1.0081 and 19.000, respectively; the additive constant in the free energy equation as -7.267; $R=1.9869$; $hc/k=1.4324$. Nuclear spin contributions have been omitted in accordance with the usual custom. It should be noted that the quantities in Table II, refer to the ideal, diatomic molecule, HF at unit activity. At temperatures below 88°C, it is known[5] that HF is associated in the gas phase and it was shown that the available vapor density data could be interpreted on the assumption that a single equilibrium exists: $6HF \rightleftharpoons H_6F_6$. Recent electron diffraction studies by Bauer, Beach and Simons,[6] however, have shown this assumption to be untenable.

For temperatures not contained in Table II, a convenient interpolation formula[7] has the form:

$$-(F^0-H_0^0)/T=a/T+b \log T+cT+dT^2+i. \quad (1)$$

Other thermodynamic functions such as entropy, heat content and heat capacity may be obtained

TABLE I. *Molecular constants of* HF *and* F_2 *(in* cm^{-1}*).*

	HF	F_2
ω_e	4141.305	856 (ω_0)
$x_e\omega_e$	90.866	—
B_0	20.542	0.839
α_e	0.7535	—
D_0	-2.20×10^{-3}	—

* This material was presented to the Division of Physical and Inorganic Chemistry of the American Chemical Society at Baltimore, April, 1939.

[1] Imes, Astrophys. J. **50**, 251 (1919).
[2] Schaefer and Thomas, Zeits. f. Physik **12**, 330 (1923).
[3] Kirkpatrick and Salant, Phys. Rev. **48**, 945 (1935).
[4] Gordon and Barnes, J. Chem. Phys. **1**, 297 (1933).
[5] Simons and Hildebrand, J. Am. Chem. Soc. **46**, 2183 (1924).
[6] Bauer, Beach and Simons, J. Am. Chem. Soc. **61**, 19 (1939).
[7] Murphy, J. Chem. Phys. **5**, 637 (1937).

from Eq. (1) by differentiation.[8] The coefficients of Eq. (1) are shown in Table III. These numbers will reproduce the values in Table II over the whole temperature range with an average deviation for the free energy, entropy and heat capacity of 0.001, 0.006, 0.050, respectively; the maximum deviations are 0.001, 0.022, 0.276. If the equation for the heat capacity is used between 298.1° and 1600° only, the average and maximum deviations become 0.018 and 0.042.

The normal state of F_2 is not known spectroscopically although electronic bands obtained in emission by Gale and Monk[9] are often erroneously believed to involve the ground state. These bands are actually a $^1\Sigma \rightarrow {}^1\Pi$ transition between two excited states. The only available information on the normal state of F_2 is an electron diffraction result of Brockway,[10] who gives for the internuclear distance, $r_0 = 1.45 \pm 0.05$A. The uncertainty is apparently an estimated outside limit, since the mean and probable error of the six measurements result in $r_0 = 1.453 \pm 0.007$A. The value, $r_0 = 1.45 \pm 0.01$A would seem a reasonable estimate for the distance and its probable error. Assuming that all of the natural constants involved are exact, the spectroscopic quantity, $B_0 = 0.839 \pm 0.012$ cm^{-1} and further assuming that Badger's rule[11] holds exactly, the fundamental vibrational frequency[12] of the molecule, $\omega_0 = 856 \pm 17$ cm^{-1}.

TABLE II.

T, °K	$-(F^0 - H_0^0)/T$	S^0	C_p^0
	HF		
298.1	34.634	41.527	6.963
300	34.677	41.571	6.963
400	36.663	43.574	6.966
500	38.207	45.130	6.969
600	39.470	46.401	6.986
800	41.467	48.420	7.065
1000	43.023	50.012	7.214
1200	44.301	51.343	7.408
1400	45.392	52.501	7.612
1600	46.346	53.531	7.812
1800	47.197	54.461	7.992
2000	47.968	55.314	8.152
	F_2		
298.1	41.488	48.576	7.522
300	41.533	48.623	7.530
400	43.594	50.844	7.912
500	45.230	52.642	8.186
600	46.594	54.151	8.373
800	48.802	56.594	8.594
1000	50.561	58.580	8.710
1200	52.024	60.119	8.777
1400	53.281	61.476	8.819
1600	54.380	62.659	8.847
1800	55.354	63.694	8.866
2000	56.243	64.637	8.880

TABLE III.

	HF	F_2	F
a	4.1838	175.5572	−754.7500
b	15.9666	16.7976	4.6445
$c \times 10^4$	−0.9207	11.017	40.380
$d \times 10^8$	7.76	−12.61	−74.70
i	−4.8676	−0.9780	22.5832

The use of these quantities alone is equivalent to considering the molecule as a rigid rotator and a harmonic oscillator. An estimate of the size of the anharmonic and stretching terms could be made with some assumed potential energy function such as that of Morse but the uncertainties in the above quantities are probably greater than the additional terms. One further uncertainty lies in the fact that the location of the excited $^1\Pi$ level is unknown relative to the ground state. It seems unlikely, however, that it could be low enough to make any contribution to the sum over states at temperatures below 2000°K.

The thermodynamic quantities calculated to this approximation are listed in Table II. The sum over states was again obtained from the tables of Gordon and Barnes. The constants of the interpolation formula for F_2 are given in Table III. The average deviations between results calculated with these numbers and the entries in Table II for the free energy, entropy and heat capacity are 0.008, 0.033, 0.12; the maximum deviations are 0.022, 0.072 and 0.36, respectively.

We have also made an estimate of the errors involved in the quantities of Table II for F_2

[8] For the explicit form of these equations, see reference 7. Eq. (2) of that paper should have a plus instead of a minus sign for the first term.

[9] Gale and Monk, Phys. Rev. **29**, 211 (1927); Astrophys. J. **69**, 77 (1929). See also Mulliken, Phys. Rev. **46**, 549 (1934), footnote 12a for some further unpublished details.

[10] Brockway, J. Am. Chem. Soc. **60**, 1348 (1938).

[11] Badger, J. Chem. Phys. **2**, 128 (1934); **3**, 710 (1935).

[12] An unsuccessful attempt to determine the vibrational frequency from the Raman spectrum of liquid F_2 was made by Garner and Yost, J. Am. Chem. Soc. **59**, 2738 (1938).

due to the uncertainties in the spectroscopic constants. With probable errors as given above and in Table I as the only errors in the summations, the probable error in the free energy is independent of temperature and is about 0.07 percent. The probable error in the entropy increases from 0.07 percent at 300° to 0.14 percent at 2000°. The heat capacity may be in error by 0.92 percent at the lower temperatures but the error has decreased to 0.37 percent at 2000°.

The sum over states for monatomic fluorine is $(4+2\exp(-407hc/kT))$, where 407 cm^{-1} is the separation[13] of the $^2P_{1/2}$ and $^2P_{3/2}$ states of the fluorine atom. The coefficients of the interpolation formula for the F atom are given in Table III.

The Dissociation of Hydrogen Fluoride

The change in free energy of the reaction:

$$\tfrac{1}{2}H_2(g)+\tfrac{1}{2}F_2(g)\rightleftharpoons HF(g) \qquad (2)$$

may be calculated from the quantities in Table II for HF and F_2 and the corresponding values for H_2,[14] provided ΔH_0^0 for the reaction is known. Direct measurements of the heat of formation of HF at room temperature have been made by von Wartenberg and Fitzner[15] and by Ruff and Laas.[16] The former have also measured the heat of reaction between F_2 and solid NaCl and have obtained a value for the heat of formation of HF by combining their result with other thermal data. These quantities were all corrected for polymerization of HF in the gas phase from the data of Simons and Hildebrand.[5] A few additional corrections by Ruff and Menzel[17] give an average result of all the experiments at room temperature of $\Delta H^0=-64{,}000$ cal./mole. A later determination by von Wartenberg and Schutza[18] was made at 100°C to eliminate the necessity of correcting for polymerization. Their result is

$$\Delta H^0_{373}=-64{,}450\pm100 \text{ cal./mole},$$

which we take for the determination of ΔH_0^0 since it is the most direct determination and in good agreement with the other investigations quoted above. An earlier measurement of Berthelot and Moissan[19] resulted in $-38{,}500$ cal. which differs so widely from the more recent measurements that it need not be considered further.

Using our interpolation formula for HF and F_2 and a similar one[7] for H_2, we obtain $\Delta S^0_{373}=1.5$ cal./mole and $\Delta F^0_{373}=-65{,}030\pm100$ cal./mole. Similarly, we obtain $\Delta(F^0-H_0^0)/T=-1.65$ at 373°K and $\Delta H_0^0=-64{,}410\pm100$ cal./mole. Combining this value with $\Delta(F^0-H_0^0)/T$ at 298.1°, results in $\Delta F^0_{298.1}=-64{,}910\pm100$ cal./mole.

The variation of ΔF^0 with temperature and the equilibrium constant for the reaction between 298.1° and 2000° is given by an equation of the form:

$$\Delta F^0=-RT\ln K=\Delta H_0^0-\Delta aT\log T-\Delta bT^2-\Delta cT^3-\Delta iT, \qquad (3)$$

where a quantity such as

$$\Delta a=(a_{HF}-\tfrac{1}{2}(a_{F_2}+a_{H_2})).$$

The numerical constants of this equation are given in Table IV. This equilibrium has been studied experimentally by Morgan and Hildebrand[20] who measured the electromotive force of a cell containing polarized electrodes immersed in molten KHF_2 at temperatures between 223° and 272°C. By combining these measurements with vapor pressure measurements of HF over the cell, they have obtained values of ΔF^0 for the reaction at their experimental temperatures. They have also obtained the standard free energy change of the reaction at 298.1°K by three different methods. Extrapolation of their experimental data gave $-32{,}500$ cal.; use of the Latimer equation[21] gave $-31{,}800$ cal. and a calculation from the entropy and the heat of reaction as measured by Berthelot and Moissan[19] gave $-33{,}600$ cal. The large discrepancy be-

[13] Bacher and Goudsmit, *Atomic Energy States* (McGraw-Hill Book Co., New York, 1932).
[14] Giauque, J. Am. Chem. Soc. **52**, 4816 (1930); Davis and Johnston, *ibid.* **56**, 1045 (1934).
[15] Von Wartenberg and Fitzner, Zeits. f. anorg. allgem. Chemie **151**, 313 (1926).
[16] Ruff and Laas, Zeits. f. anorg. allgem. Chemie **183**, 214 (1929).
[17] Ruff and Menzel, Zeits. f. anorg. allgem. Chemie **198**, 375 (1931).
[18] Von Wartenberg and Schutza, Zeits. f. anorg. allgem. Chemie **206**, 65 (1932).
[19] Berthelot and Moissan, Ann. chim. phys. (6) **23**, 572 (1891).
[20] Morgan and Hildebrand, J. Am. Chem. Soc. **48**, 911 (1926).
[21] Latimer, J. Am. Chem. Soc. **43**, 824 (1921).

TABLE IV.

	$\frac{1}{2}H_2+\frac{1}{2}F_2 \rightleftarrows HF$	$F_2 \rightleftarrows 2F$
Δa	−85.1656	−1685.0572
Δb	−0.2322	−7.5086
$10^4\times\Delta c$	−7.052	69.743
$10^8\times\Delta d$	+12.20	−136.79
Δi	+2.7280	46.1444
ΔH_0^0	−64,410±100	63,300

tween these results and our calculated value is difficult to understand but may be due to a highly irreversible electrode process in the cell measured by Morgan and Hildebrand.* Jellinek and Rudat[22] have also concluded that Morgan and Hildebrand's experimental values are too low from approximate values of ΔS^0 and ΔH^0.

Jellinek and Rudat[22] have measured experimentally the equilibria at temperatures between 100° and 800°C for the reactions: $XF_2+H_2 \rightleftarrows 2HF+X$ where X was a large number of metals. They have used approximate values of the equilibrium constant for the dissociation of HF to calculate the dissociation pressure of these metallic fluorides. Their results are in good agreement with more exact calculations using our Eq. (3).

Domange[23] has measured equilibria in the systems: $XF_2+H_2O \rightleftarrows XO+2HF$ and in the cases where his temperatures overlap with those of Jellinek and Rudat, equilibrium constants may be calculated for the reaction: $X+H_2O \rightleftarrows XO+H_2$. There is enough additional information available in some cases also to calculate the dissociation pressure of the metallic fluorides or the metallic oxides from the measured equilibria of Domange. Because of the fragmentary nature of this data, we do not make the calculations here.

THE DISSOCIATION OF FLUORINE

The change in free energy for the reaction:

$$F_2 \rightleftarrows 2F \qquad (4)$$

may be calculated from the quantities in Table II for F_2 and the similar quantity for F atom provided the value of ΔH_0^0 is known. The generally accepted value of $\Delta H_0^0 = 63{,}300 \pm 700$ cal./mole was obtained by von Wartenberg, Sprenger and Taylor,[24] who determined the maximum in the ultraviolet continuous absorption of F_2 experimentally. The wave-length of convergence of vibrational levels, corresponding to dissociation could not be observed but an extrapolated value was obtained from known maxima and convergence limits in Cl_2, Br_2 and I_2 by assuming a linear variation of the difference in these two wave-lengths with atomic number. As pointed out by Mulliken,[25] however, this extrapolation has no theoretical basis nor does the supposed linear variation have any experimental basis if more recent data on the other halogens is used. Mulliken believes that the value quoted above happens to be nearly correct although the indicated error is too small. Bodenstein, Jockusch and Chong[26] have also determined the maximum in the absorption of F_2 but fail to find the convergence limit. They prefer to plot the known heats of dissociation of the other halogens and of hydrogen against atomic number and interpolate for F_2 obtaining 70,000 cal./mole. They have, however, used for the heat of dissociation of hydrogen, a value considerably lower than the present accepted value[27] of 102,700 cal./mole and consequently their method should give a result still higher than the value that they have determined. There is, moreover, no theoretical justification for their procedure. The highest value reported[28] is 76,000±2000 cal./mole which was obtained from the absorption spectra of NaF and KF.

Electron affinity data have also been extrapolated by various investigators, Lederle,[29] for example obtaining, 66,800 cal./mole. A resume of earlier estimates by various investigators is given by Bichowsky and Rossini[30] who take

* In a personal communication from Professor Joel H. Hildebrand of the University of California, he has given us permission to state that subsequent studies have indicated that Morgan and Hildebrand were dealing with a polarization potential which did not correspond to the process that they thought they were studying.

[22] Jellinek and Rudat, Zeits. f. anorg. allgem. Chemie **175**, 281 (1928).

[23] Domange, Ann. chim. **7**, 225 (1937).

[24] Von Wartenberg, Sprenger and Taylor, Zeits. f. physik. Chemie, Bodenstein-Festband, 61 (1931).

[25] Mulliken, J. Chem. Phys. **2**, 782 (1934); see, in particular, footnote b, pp. 792–3.

[26] Bodenstein, Jockusch and Chong, Zeits. f. anorg. allgem. Chemie **231**, 24 (1937).

[27] Beutler, Zeits. f. physik. Chemie **B29**, 315 (1935).

[28] Desai, Proc. Roy. Soc. (London) **A136**, 76 (1932).

[29] Lederle, Zeits. f. physik. Chemie **B17**, 353 (1932).

[30] Bichowsky and Rossini, *Thermochemistry of Chemical Substances* (Reinhold, 1937).

62,600 cal./mole as the average value. None of the extrapolated values have theoretical support and very little experimental support.

It would be possible to calculate this quantity if the heat of dissociation of HF into atoms were known. Kirkpatrick and Salant[3] have estimated this to be 140,000 cal./mole from their values of ω_e and $x_e\omega_e$, assuming a Morse function. If this value is combined with our result for the dissociation of HF into molecules and Beutler's[27] value for the dissociation of H_2 into atoms, we obtain 48,400 cal./mole for the dissociation of F_2 into atoms, a result considerably lower than any of the extrapolated values. On the other hand, if we take one of the extrapolated values, 63,300 cal./mole, for example, and calculate the energy of dissociation of HF into atoms, we obtain 147,400 cal./mole, a value somewhat higher than that of Kirkpatrick and Salant. In general, an energy of dissociation calculated from the Morse function is an upper limit to the true value. There is no reason to doubt the correctness of the value for H_2 obtained by Beutler or the one above for the dissociation of HF into molecules so that there is apparently some rather large error in the extrapolated values for F_2 or the value of Kirkpatrick and Salant or both.

For purposes of calculation, we take 63,300 cal./mole for ΔH_0^0 and thus obtain an equation similar to Eq. (3) for the dissociation of F_2 into atoms. The numerical coefficients are given in Table IV. The free energy change so obtained is very uncertain due to the large uncertainty in ΔH_0^0. We should like to emphasize that there is at the present time no trustworthy value for this quantity.

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Melting as an Order-Disorder Transition

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In this paper the breakdown of a regular crystal pattern is studied for an atomic crystal of the diamond type. For practical reasons, the forces between the atoms are idealized into potential wells. It is then possible to study the motion of a limited number of particles. The lattice structure is introduced as long distance order in the manner developed by Bethe. The results show the existence of a phase transition where this long range order breaks down. Considerable thermodynamic inconsistencies are detected, however, and the reasons for these discrepancies are discussed.

1. INTRODUCTION

AT the present moment, our understanding of the two main phase transitions occurring in nature, melting and condensation, is very incomplete. This is due to two facts. On the one hand, no satisfactory treatment of the liquid phase has been developed yet. On the other hand, there is a general difficulty to understand the existence of sharp phase transitions from present-day statistical mechanics.

However, in recent years the situation has improved considerably. Mayer and others[1] have been able to prove that for every pressure there is a definite transition temperature from liquid to vapor, and they have been able to connect its position with the properties of the saturated vapor itself.

Similar progress has been made in the treatment of the superstructure of alloys. At a certain temperature a transition from order to disorder takes place in certain alloys, and this transition has been accounted for first phenomenologically and later in an atomic theory.[2] Unfortunately the methods used are much less rigorous: They

[1] J. E. Mayer, J. Chem. Phys. **5**, 67 (1937); J. E. Mayer and Ph. G. Ackermann, J. Chem. Phys. **5**, 74 (1937); B. Kahn, Diss. Utrecht; J. Frenkel, J. Chem. Phys. **7**, 200 (1939).

[2] W. L. Bragg and E. J. Williams, Proc. Roy. Soc. **A145**, 699 (1934); **A151**, 540 (1935); **A152**, 231 (1935). H. A. Bethe, Proc. Roy. Soc. **A150**, 552 (1935); F. C. Nix and W. Shockley, Rev. Mod. Phys. **10**, 1 (1938).

consist essentially in describing first the various stages of the phenomenon through one or more parameters and then giving to that simplified problem a statistical or thermodynamic treatment. In the case of superstructure the parameter is called the degree of order. It varies from 1 to 0, as we proceed from the complete superstructure to random distribution of the two components of the alloy.

There is some similarity between the transitions just mentioned and the solid-liquid transition. Actually melting is the most common passage from order to disorder and at the same time the most fundamental. In the theory of superstructures we have just two kinds of lattice sites which become equivalent as disorder sets in. Melting, on the other hand, destroys those lattice sites themselves and makes all positions in space equivalent to each other.

In spite of this it is possible to find a definition of order which is closely analogous to the one proposed by Bragg and Williams. Let us take an atomic crystal as an example. At full order, the atoms are limited to a region around the lattice points whose size is given by the zero vibration of the atoms (see Fig. 1). At full disorder, all regions in space are equivalent. Long distance order is thus linked up with the probability to find the atoms in those narrow regions. When this probability is unity the degree of order is unity; when the probability has dropped to its pure chance value, long distance order is zero.

Following Bethe, we supplement this long range order by a short distance order. For this purpose, a small part of the substance containing a few atoms only is considered explicitly; the motion of the atoms in their mutual field of force is studied. This brings in an eventual local order whose range is limited, however, by the number of atoms considered.

As an objection to this analogy it is said sometimes that the breakdown of local order cannot be the mechanism responsible for melting because the number of interstitial atoms is very small for most crystals, even if we are close to their melting point. This statement, while correct, does not constitute an argument against the calculations that follow. It is true that their framework contains the possibility that the breakdown of long range order is preceded by a large decrease of local order. But this need not be so by any means. We may find on the opposite that it is almost impossible for local disorder to develop as long as long range order persists. In this case we would find an appreciable number of interstitial atoms only in the molten phase and even there a good deal of local lattice structure may be maintained. It would be more correct then to say that the breakdown of the lattice frame "causes" a decrease in local order than the other way round. We shall see that this is actually the case realized in practice.

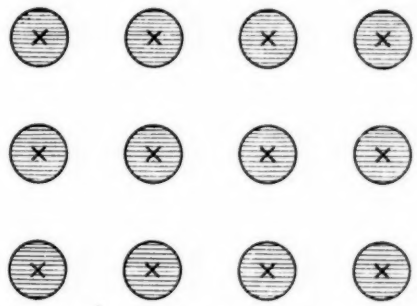

FIG. 1. Tentative definition of order for the melting process. The crosses represent lattice sites and the shaded areas the extension of the zero vibration. The latter are therefore "right" regions and the rest of space is "wrong."

2. SKETCH OF THE CALCULATIONS

Since we want to study the motion of a number of particles in their mutual field of force our choice of forces is very limited. We are actually compelled to choose them in such a way that no integration over internal degrees of freedom is necessary. As a consequence they will be of the directed valency type. The problem gains further in simplicity if the coordination number is chosen low. The lowest possible value is four. The forces then resemble the ones in carbon, quartz or ice. In consequence, we may think of the crystal structure as being of the diamond type.

The forces which we assume to exist between the atoms are best explained by the chemist's model of balls and sticks. Each atom is represented by a ball which can carry sticks of length a in the four directions of a tetrahedron; at the end of such a stick another atom can be placed and whenever a stick links two atoms together an energy W is gained. This description, however, is not precise enough for our purpose because we

must know how much play there is in such a bond between two atoms. The following assumptions have been adopted: Taking one of the atoms to be rigidly fixed we assume that the other can move freely within a volume of the shape of a penny. This penny shall lie perpendicular to the line joining it to the fixed atom and at a distance a from it. Let its thickness be d and its diameter d'. Then we choose numerically

$$d=0.1a$$
$$d'=0.4a.$$

For a and W, no numerical choice is needed; their value will affect the temperature and volume scale only.

Since we assumed that the particles are atoms we are not concerned with their energy of rotation. Furthermore, if quantum phenomena are neglected the kinetic energy of translation is $\frac{3}{2}kT$ per atom, independently of the state of order. Thus melting depends only on the mutual potential energy of the atoms in the crystal.

With the help of the data furnished it is possible to predict the change of energy and entropy which we must find when we go from a completely ordered and unstrained state of the substance into a fully disordered and highly expanded arrangement. In a completely ordered state every atom is in the attractive well of its four neighbors and the volume v within which it can move freely is limited accordingly. In the disordered and expanded state they form an ideal gas and are out of each other's field of force. Thus, leaving out the contributions due to the kinetic energy, we get for the energy change per atom:

$$\Delta E=2W \tag{1}$$

and for the entropy change

$$\frac{\Delta S}{k}=\frac{1}{N}\log\frac{(NV)^N}{N!v^N}, \tag{2}$$

where k is Boltzmann's constant, N the number of particles considered, V the volume per atom in the ideal gas state and v the volume accessible to an atom in the completely ordered arrangement. A good approximation to the value of v can be obtained by using the "Einstein model" of the solid, i.e., by putting all atoms on their lattice

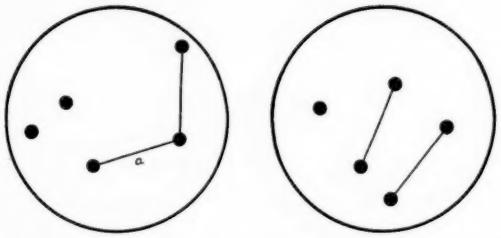

FIG. 2. Arrangements of energy $-2W$ for five carbon-like atoms. The black dots represent atoms and the lines bonds between them.

points except one, which we let move about its own lattice position. From the force constants and the lattice structure we find thus for v:

$$v=(\sqrt{3}/2000)a^3.$$

Since a is the equilibrium distance between two nearest neighbors we can replace a^3 by the volume V_0 per atom for the unstrained crystal. We find for the diamond structure

$$V_0=(8/3\sqrt{3})a^3.$$

If we put in these two expressions and use Sterling's formula for the factorials we can write (2) in the form

$$\Delta S/k=7.62+\log V/V_0, \tag{2a}$$

if N is taken to be infinite. We shall need later the value for $N=5$. It is

$$\Delta S/k=7.27+\log V/V_0. \tag{2b}$$

These values are somewhat higher than they are for actual substances because our forces between the atoms are rather tight. But there is no reason to believe that wider potential wells would upset the calculations fundamentally.

In Bethe's method relation (1) is an identity. Relation (2) on the other hand can be used as a check for the correctness of the method.

In the method itself we restrict ourselves to the study of five atoms, a central one and its four immediate neighbors. These five particles are hemmed in by the other atoms; we take this into account by letting them move in a sphere whose (variable) volume is taken to be five times the atomic volume.

In the absence of long range order we simply analyze the motion of these five atoms. They can form among each other arrangements whose

potential energy is, respectively, $-4W$, $-3W$, $-2W$, $-W$, 0. As an example let us study the arrangement $-2W$ (Fig. 2). It consists either of two free atoms and the three others forming a triangle or else one free atom and two double molecules. In order to form a partition function we have to compute the weight of such an arrangement. Call the radius of the sphere R. Then we get a factor $4/3\pi R^3$ for each free atom. In the case of the triangle, we do not get quite as much for its degree of freedom of translation; we have to take instead the volume common to three spheres of radius R whose centers are placed in the same mutual position as the three atoms of the triangle. We denote this volume by $4/3\pi R^3 f_\Delta$. Once this reduction is carried out the internal degrees of freedom of the triangle may be treated as free. One finds for their weight:

$$(4\pi a^2 d)\left(\frac{4\pi\sqrt{2}}{3} add'\right).$$

In addition, the whole weight has to be multiplied by 30 because there are 30 ways to distribute 5 atoms in such an arrangement. Thus the full weight is

$$30\left(\frac{4}{3}\pi R^3\right)^2 f_\Delta (4\pi a^2 d)\left(\frac{4\pi\sqrt{2}}{3} add'\right).$$

Similar expressions can be obtained for all other arrangements.

There is one difficulty which should be mentioned at this point. We should expect that at low temperatures the atoms form a tetrahedral structure which is the arrangement of 100 percent short range order. This is not true in our model because they can form a chain of five which has the same energy and a higher entropy. Actually, chain-like arrangements have a much lower binding energy; this becomes obvious if more than five particles are explicitly treated in the problem. But in this first approximation the arbitrary rule had to be adopted that arrangements which cannot be obtained by decomposition of the original tetrahedron shall not be included in the state sum.* This means for example that the second arrangement of Fig. 2 is not included.

It is interesting to compare this part of the calculation with the work of Mayer, Kahn and Frenkel.[1] We want to identify later the state of vanishing long range order with the fluid (liquid or gaseous) phase. Actually we study the gradual dissociation of a molecule of five atoms. The authors mentioned have shown that evaporation is nothing else but just such a dissociation process, except that the molecule is a giant containing millions of atoms. It follows that that part of the calculation which does not include long range order is in one sense a very clumsy approximation to a correct treatment of boiling. In another sense it is more refined because our liquid phase has a structure, namely the same local structure as the crystal. Fig. 3 shows the p-V-isotherms resulting in comparison with the ideal gas curves. In the upper part, both thermal expansion and compressibility are reduced by about the right amount, but towards the bottom the curves go flat, showing a washy kind of evaporation. They must go wrong there, of

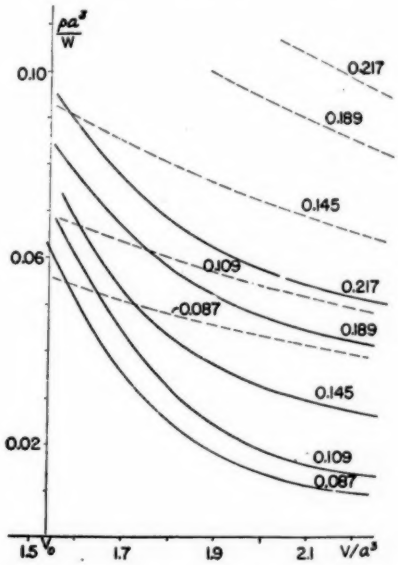

FIG. 3. Pressure-volume isotherms for the model fluid (————) and for an ideal gas (– – – – –). V_0 is the volume of the (nearly incompressible) solid phase, a^3 and W parameters of the model. The values of kT/W are given on the curves.

* For purposes of information, calculations which do not impose this restriction have been carried out too. The solid phase is practically the same as in the text, but the unstable and the liquid branch in Fig. 6 are shifted upwards. As a consequence one gets an entropy change which is smaller than (6); this makes the disagreement with (2) even worse.

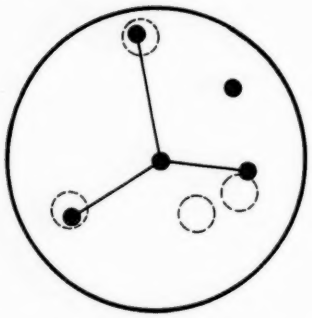

FIG. 4. An arrangement of energy $-(3W+2U)$. Four out of the five atoms form a tripod and two ends of the tripod are in holes due to long range order (marked as circles). The third is just somewhat outside.

course, because in a five-particle model, the pressure cannot fall below $\frac{1}{5}$ of the ideal gas pressure. Actually these are the only interesting pressures because our unit W/a^3 is of the order of Young's modulus for the solid. Thus the whole treatment is restricted *a priori* to very high pressures.

Our real problem begins only with the introduction of long distance order. This concept can be brought into the calculation in a fashion strictly analogous to the one used by Bethe in his treatment of superstructure. The previous calculation underestimated the probability for a regular arrangement of the five particles because it neglected the fact that if the outside forms a regular pattern it influences the inside in the same direction. We assume therefore that there are four equilibrium locations in the sphere which can be occupied by one atom each, and whenever such a site is occupied an energy U is gained.

We assume that these holes are placed in such a way that our tetrahedron just fits in naturally for the volume $V=V_0$ (V_0=atomic volume at absolute zero under no strain); but if the volume V is increased or decreased their placement follows the deformation which gives rise to a severe stress. This is a natural assumption because they stand for the effect of three atoms outside the sphere which move out as soon as V goes up. From this same analogy we can compute their size and again for this reason we must assume that an atom which occupies such a site has only one "valency" left which points rigidly towards the center. The analogy would be complete if we took the depth U of the holes as $3W$, but we shall keep this quantity as a free parameter which will be determined later.

There are now 25 arrangements making up the state sum. Their energies are given by all possible combinations $-(nW+mU)$ where m and n vary from 0 to 4. Again the weights are given by geometric reasoning. Fig. 4 shows as an example one of the two arrangements whose energy is $-(3W+2U)$. Call the size of the potential wells due to long range order S and assume we are studying the unstrained volume $V=V_0$. Then we have for the weight in question

$$1440\left(\frac{4}{3}\pi R^3\right)S^2\left(\frac{\sqrt{3}}{4\pi}d^2d'\right)\left(\frac{1}{4\sqrt{6}}dd'^2\right).$$

The first factor gives the number of possible arrangements, then follows the contribution of the free atom, then the two particles in the wells, then the central atom, then the atom which is linked to the central one, but not contained in the corresponding well.

The value of U has been kept open so far. We determine it now by imposing the crystal symmetry upon our five-particle problem. In this

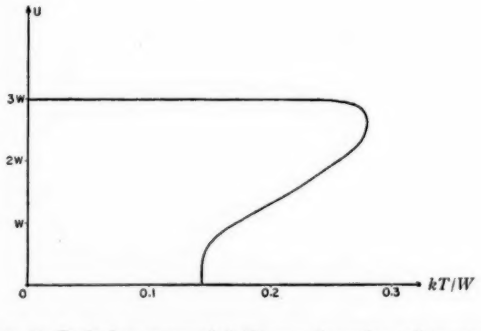

FIG. 5. Ordering potential U as a function of temperature. Compare the strict constancy of U with the slight decrease of $-E$ in Fig. 6. Thus, a slight thermal agitation cannot damage the lattice structure.

problem there has been a natural distinction between the central atom and the outside ones; but in reality all statements about them should be symmetric. This is not the case for individual arrangements in the state sum. The arrangement of Fig. 4, e.g., has a probability 1 for the central lattice site to be occupied while this value is only $\frac{3}{4}$ for the outside ones. But we can dispose of U to make the two probabilities equal for the full state sum. Thus U becomes a function of T

and V. In Fig. 5 we see it plotted for the constant volume $V=V_0$ as a function of temperature. The volume dependence itself is very slight. Besides this solution there exists of course always the solution $U=0$.

We are now in the possession of a partition function $f(T, V)$ of the form

$$f(T, V)=\sum_{n,\, m=0}^{4} \tilde{\omega}_{nm}(V) \exp\left(\frac{nW+mU(T, V)}{kT}\right). \tag{3}$$

At this point, a very delicate question arises which is rather rapidly glossed over in some treatments of order-disorder transitions. The function (3) is of a statistically incorrect structure since some of the Boltzmann exponents depend on temperature not only through $1/T$. In consequence there are several "energies" which might be computed from it, e.g.

$$\frac{1}{f(T, V)} \sum_{n,\, m=0}^{4} \tilde{\omega}_{nm} nW \exp\left(\frac{nW+mU}{kT}\right),$$

$$\frac{1}{f(T, V)} \sum_{n,\, m=0}^{4} \tilde{\omega}_{nm} mU \exp\left(\frac{nW+mU}{kT}\right),$$

$$kT^2 \frac{\partial \log f(T, V)}{\partial T}.$$

In accordance with Bethe, the first expression has been chosen because it links up rather closely energy and short distance order. But the usual expression for the free energy is then not valid and we have to compute it from thermodynamics; this is done with the formula

$$-\frac{F}{kT}=\log V+\frac{1}{k}\int_{\infty}^{T} \frac{E}{T^2} dT. \tag{4}$$

The integral on the right-hand side can be used in the standard way to determine the transition temperature between two phases which are joined by an unstable loop. This is at least so if the work of expansion at the transition point can be neglected in comparison with the energy change. We shall refer to this procedure later as "the law of equal areas."

Once F is obtained entropy and pressure follow easily from the relations

$$S=(E-F)/T$$
$$p=-\partial F/\partial T. \tag{5}$$

3. Results

In Fig. 6, the binding energy per molecule (crystal energy) is plotted as a function of temperature. The plot is taken at constant volume, namely the stable volume of the solid at absolute zero and zero pressure. A constant pressure graph looks very much the same; the differences will be discussed later.

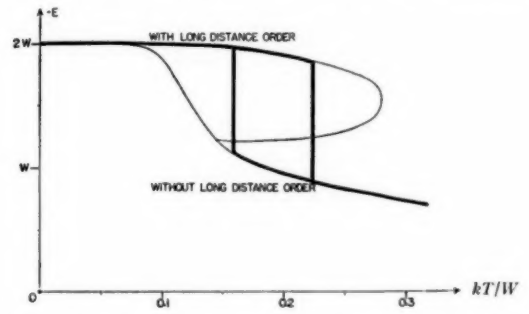

FIG. 6. Binding energy per atom (crystal energy) as a function of temperature for the solid and "fluid" phase. The melting point on the right is computed with the "law of equal areas," the one on the left by separate thermodynamic treatment of each phase.

Disregarding first the two vertical lines in Fig. 6, we see that the curve consists of two branches. The lower one is the liquid-gas curve and shows a gradual decrease in binding. The top curve represents the solid phase and shows the characteristic loop which we associate with a phase transition. For its stable part, the potential due to long distance order is practically a constant (see Fig. 5) and the binding energy decreases only very slowly with temperature. The loop which follows does obviously not describe the most stable arrangement and a phase transition must take place at the temperature where the free energies of the two phases are equal (since we are discussing an idealized "constant volume" transition). Assuming the law of equal areas to be correct we get a melting point

$$kT/W=0.222.$$

This transition temperature is indicated by the vertical line on the right-hand side of the graph.

We can, however, use the integration (4) also as a check of the method. If the calculation is correct the total entropy change from the fully ordered into the gaseous phase must be the same as the one obtained *a priori* (formula (2b)). Since the disordered phase goes over correctly into an ideal gas at large volumes we find the correct volume dependence. The numerical constant is not so good though, for we find

$$\Delta S/k = 5.55 + \log V/V_0, \tag{6}$$

which is a disagreement of about two units. Another way of showing up the same discrepancy is chosen in Fig. 6, where a second transition point has been drawn. It has been obtained by disregarding the law of equal areas and computing the free energy separately for each phase. The numerical value of this temperature is

$$kT/W = 0.157.$$

The two melting points differ from each other by about 40 percent.

It is well possible that an inclusion of more atoms in our treatment would close this gap. This can be made plausible by the following reasoning: When we are doing statistics on a limited amount of matter the total entropy increases with the number of particles involved and the total potential energy with the number of bonds between them. The true ratio between particles and bonds in a diamond-like lattice is $\frac{1}{2}$. In our model, however, this ratio is 5/4. Consequently, we are overestimating the entropy of the ordered arrangement if we normalize the energy to fit the facts. This, in turn, will yield too small a value for the entropy increase on melting and evaporation.

Such a reasoning does not explain why the entropy check is so good in the case which was treated originally by Bethe.[2] The present results differ from his chiefly through that large unstable loop which links up the two phases. Such a loop has been found by Peierls in his work on the alloy AB_3.[3] Unfortunately he has not carried out the entropy check for his data. But it is the authors experience that the unstable branch is more sensitive to changes in the weights than any other section and hence that part is more uncertain. This view is confirmed by another feature: this unstable branch is just the part where U depends strongly on temperature (Fig. 5) and, as a consequence, the partition function becomes statistically incorrect.* In Bethe's case this bad stretch of curve is extremely short and can have very little influence on an integration. It is perhaps significant that this is also the region with a low degree of long range order, as defined by Bragg and Williams. Such states are extremely improbable because they correspond to an arrangement where a small fraction of the atoms is placed according to a regular long distance pattern while the remainder does not bother about it. Since the chance for such a situation is obviously very small it is doubtful whether they are states of maximum entropy. If they are not, formula (4) and the law of equal areas do not apply to them.

It has been remarked at the end of Part 1 that we should find a rather large amount of local order maintained throughout the melting process. In this respect the solid phase is completely satisfactory. On Fig. 6 there is a decrease of binding energy noticeable below the melting point. But an atom can only leave its lattice site if all four bonds which link it up with the rest of the crystal are broken. This is indeed a very rare event; the probability of its occurrence is roughly equal to the fourth power of the probability that a single bond is broken. More exactly, one finds for the value of this probability 10^{-7} at the lower melting point and 10^{-4} at the upper one. This same behavior is reflected by the strict constancy of U throughout the solid phase (Fig. 5).

It must be admitted that the liquid phase is less satisfactory in this respect. The amount of potential energy left after melting is larger than in the case of superstructure, but it is not large enough. We see from Fig. 6, that about half the crystal energy is released on melting which leaves about the same amount for evaporation. In reality the latter quantity is considerably larger. This shortcoming is due to the fact that our fluid is something between a liquid and a gas. It is clear from the work of Mayer and others[1] that if we included a large number of particles in our treatment the fluid would be clearly liquid or gaseous and so this trouble would be mended.

[3] R. Peierls, Proc. Roy. Soc. **A154**, 207 (1936). See also F. C. Nix and W. Shockley, Rev. Mod. Phys. **10**, 13 (1938).

* See page 815.

The results at constant pressure differ very little from the ones at constant volume if the pressure is chosen sufficiently high. The solid phase may well be treated as incompressible because both thermal expansion and compressibility are extremely small. The reason for this is of course the extreme rigidity of the forces.

The constant pressure data for the liquid phase is rather different. They show an accelerated rate of thermal expansion because the liquid goes over continuously into the gaseous phase; thus almost any positive value can be obtained for the volume increase on melting. As long as it is kept small, Fig. 6 remains very much as it is; but if the pressure is low, the liquid becomes more like a gas, its binding energy drops and the transition temperature moves up.

It should be mentioned at this point that the reasonable results just described are obtained only if the law of equal areas is definitely discarded as far as the pressures are concerned. It has been mentioned above that this law does not agree with the entropies obtained separately for each phase. From Eq. (5) it follows that such an error gives rise to spurious pressures in one or the other of the two phases. It must be said that these contributions would lead to errors rather worse than the ones discussed up to the present.

4. Conclusion

Although the method used is not likely to be of value for quantitative purposes, it has been able to show up some qualitative facts about the melting process. First of all, it does establish firmly that the sharp melting point is due to the breakdown of crystalline long distance order. This is of course also a well-known experimental fact; amorphous solids show only a gradual softening, but crystals have a definite melting point. Secondly the calculation shows the intimate connection between order-disorder transitions in alloys and melting. The former appears as a very restricted type of breakdown of order, while the latter is its most radical form. It does prove also that the repulsive forces between atoms and the harmonic character of their attraction is only of secondary importance for the process. In addition, melting temperature and latent heat come out of the right order of magnitude.

The quantitative shortcomings have been discussed in Part 3; they are connected to a great extent that we deal with two phases which join each other through an unstable loop. It is probable that the results would improve if the number of atoms treated explicitly were increased. But it cannot be judged from the present work whether a satisfactory limit could be reached with a reasonable number of particles.

Finally I want to express my thanks to Professor G. Breit whose suggestions have been very valuable for the set-up of the problem. I also want to thank Professor N. F. Mott and Dr. L. P. Bouckaert for valuable discussions.

Optical Surface Thickness of Pure Water

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An apparatus and method is described, based on the optical theory of Drude, capable of measuring surface film thickness of less than a monomolecular order of magnitude. The retardation in phase sustained by plane polarized light at a transparent reflecting surface is compensated and measured by tension on a thin glass microscope cover slip. The method is applied to pure water and the results indicate that the least possible thickness of the water surface is 2–3A. The ellipticity from water at the polarizing angle is estimated by two observers to be 33×10^{-5} and 42×10^{-5}.

WHEN plane polarized light is reflected from the surface of a transparent dielectric it suffers changes in amplitude and phase. The approximate laws governing these changes were first deduced by Fresnel who assumed perfectly sharp transition at the reflecting surface. That this assumption cannot be strictly valid may be realized by considering the following physical conditions all of which are of general occurrence in nature: (1) Ridges and hollows, in solids, small compared with the wave-length of light, (2) thermal vibration, (3) surface zone differing physically from the interior bulk phase, and (4) sorbed layers on unsaturated surface valencies.

There have been a number of attempts to amplify Fresnel's theory to include the effect of a transition layer between the two media. Of these the one most generally accepted is that of Drude[1] whose formulation has been substantiated by independent derivation of Maclaurin.[2,3] Drude's equation for the relation between the angle of incidence, i, and the phase difference, Δ, is the following:

$$\tan\Delta=\frac{4\pi}{\lambda}\frac{\mu_2^2/\mu_1}{\mu_1^2-\mu_2^2}\frac{\sin i\tan i}{\tan^2 i-\mu_2^2/\mu_1^2}\times\int_0^l\frac{(\mu^2-\mu_1^2)(\mu^2-\mu_2^2)}{\mu^2}dz, \quad (1)$$

where Δ is the retardation in phase of the component perpendicular to the plane of incidence behind the parallel component after reflection of plane polarized incident light, i is the angle of incidence, μ_1 is the index of refraction of the first medium through which the light passes, μ_2 is the index of refraction of the second medium, λ is the wave-length in vacuum, z is the direction normal to the reflecting surface, l is the thickness of the transition layer, and μ is the refractive index of the transition layer.

From Eq. (1) it may be seen that at the polarizing angle, where $(\tan^2 i-\mu_2^2/\mu_1^2)$ is zero, Δ is $\pi/2$. Accordingly, as a consequence of Drude's theory, at the polarizing angle and in its immediate vicinity, we would expect to find measurable elliptical polarization after reflection. The extent of this ellipticity is dependent on the physical nature of the sorbed or transition layer.

For the case at the polarizing angle where Eq. (1) becomes $\tan\Delta=\infty$, Drude derives

$$\bar{\rho}=\frac{\pi}{\lambda}\frac{(\mu_1^2+\mu_2^2)^{\frac{1}{2}}}{\mu_1^2-\mu_2^2}\int_0^l\frac{(\mu^2-\mu_1^2)(\mu^2-\mu_2^2)}{\mu^2}dz, \quad (2)$$

where $\bar{\rho}$ is the ratio of minor and major elliptical axes.

It may be seen from Eqs. (1) and (2) that if μ of the transition layer is not constant throughout its depth, its manner of variation must be known for l to be evaluated from experimental data of Δ and i or of $\bar{\rho}$ and i.

One modern conception of a transition layer is that of a sorbed monomolecular layer in which it might be permissible to assume that μ is constant. Eq. (1) would thus become

$$\tan\Delta=\frac{4\pi l}{\lambda}\frac{\mu_2^2/\mu_1}{\mu_1^2-\mu_2^2}\frac{(\mu^2-\mu_1^2)(\mu^2-\mu_2^2)}{\mu^2}\times\frac{\sin i\tan i}{\tan^2 i-\mu_2^2/\mu_1^2}. \quad (3)$$

[1] Drude, *Theory of Optics* (1902), page 292.
[2] Maclaurin, Proc. Roy. Soc. **A76**, 49 (1905).
[3] Bruce, "Optical Thickness of the Transition Layer between Transparent Media," Proc. Roy. Soc. **A171** (1939). (In press.)

It is obvious that l and μ cannot be gotten separately by simultaneous solution of Eq. (3). To ascertain l, either μ must be known or a value assumed. When $\mu_1<\mu<\mu_2$ the least possible value for l consistent with given data for Δ and i is obtained by assuming $\mu^2=\mu_1\mu_2$.

General Experimental Procedure

In the present work it was attempted to ascertain the optical thickness of the surface layer of pure water, by measuring Δ at known values of i at and near the polarizing angle, utilizing Drude's theory by assuming a reasonable value for μ. Briefly, the method is as follows: A beam of plane polarized light is directed onto the surface to be studied. Upon reflection this beam is not plane polarized, as deduced by Fresnel, but elliptically polarized because of the existence of a finite surface transition layer. The reflected beam is passed through a variable compensator which alters the relative phases of the two components. The compensator is varied just sufficiently to bring the ellipse back to the state of plane polarization as determined by minimum transition through an analyzing Nicol prism. This point of minimum transition is determined photographically. The variable compensator had previously been calibrated to give directly the phase retardation, Δ. The angle, i, is measured. Then, knowing λ, μ_1, μ_2, and assuming a value for μ, the surface film thickness, l, remains as the only unknown in Eq. (3).

In the case where i has the value of the polarizing angle, Eq. (2) is utilized, $\tilde{\rho}$ being calculated from the equation

$$\tilde{\rho}=\frac{\tan 45^\circ}{\tan\alpha}\tan\frac{\Delta c}{2}, \qquad (4)$$

where α is the azimuth of the polarizer, measured from the plane of reflection, and Δc is the phase difference for the ellipse when referred to the compensator axes set at an azimuth of 45°.

Apparatus

The experimental arrangement is represented in Fig. 1. A is the light source, a water-cooled mercury arc designed[4] to produce intense and

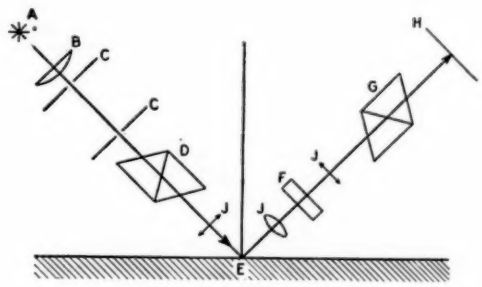

FIG. 1.

constant illumination. B is a fused silica collimating lens. C, C, are parallel slits. D is a polarizing Nicol. E is the reflecting liquid surface under investigation. F is the variable compensation plate. G is the analyzing Nicol. H is a photographic plate. J, J, J, indicate the states of polarization of the incident, reflected, and compensated light beams.

The apparatus was assembled in four parts, (1) the light with its housing and controlling rheostats, (2) the collimating lens, slits, and polarizing Nicol, (3) the container for the experimental liquid with its housing for temperature and humidity control, and (4) the compensator plates, analyzing Nicol and camera. The last three of these units were mounted on heavy metal standards milled to slide along grooves in a heavy metal base in such a way that their center axes always remain in the same vertical plane as the three units are altered in position. All units were mounted on a vibrationless pillar separated from the floor and walls of the room. The whole apparatus was located in a room which could be completely darkened, and the various parts were shielded by black felt curtains from stray light. Fig. 2 is a photograph of the apparatus.

The current through the arc and the voltage across were carefully controlled by slide rheostat resistances. It was found necessary to maintain the cooling water of the arc light bath at very constant level.

The slits of the collimating unit were adjustable, but in practice were held horizontal at 1 mm width. They were fixed at 31 cm apart. The slit-

[4] Harrison and Forbes, J. Opt. Soc. Am. **10**, 1 (1925); J. Am. Chem. Soc. **44**, 2449 (1925). More recent experiments with the Bol (C. Bol, "A New Mercury Arc," De Ingenieur **50E**, 91 (1935)) mercury arc light show it to be vastly superior to the type used in this investigation. The Bol light was found to be about 57 times the more intense and therefore not only shortens the time of exposure but also permits the use of filters.

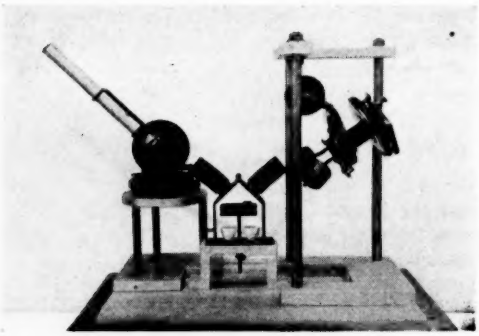

FIG. 2.

tube was attached to a disk with graduated scale and vernier on its periphery for determination of the angle of incidence. The polarizing Nicol, seen at the lower end of the slit-tube in Fig. 2, could be swung out of the path of the light beam but was mechanically so arranged that it could always be returned precisely to its original position. This Nicol and its companion analyzer were exceptional crystals, extremely clear, of large aperature, and nearly free from flaws. Small set screws permitted both polarizer and analyzer to be clamped at any desired azimuth.

The reflection chamber is represented in Fig. 3. The liquid from which reflection takes place is held in *E*, a small glass trough liberally coated with paraffin blackened with lampblack. The light passes to and from the chamber through windows, *Q*, consisting of microscope cover glasses selected for their freedom from strain. These windows are cemented onto sylphon bellows which permit adjustment of the windows at right angles to the beam, thus serving to minimize their effect on the polarization of the light. *T*, *T* are crucibles filled with the same liquid as *E*, helping to saturate the atmosphere in the chamber. *F* is a strip of brass, coated with black paraffin, used to block light reflected from the floor of the dish, *E*. The hole at the top of the chamber was used for pipetting. The front and back of the chamber, parallel to the plane of the paper, consisted of glass plates clamped on. A little stopcock grease was used to make the apparatus air-tight.

The compensator, analyzer, and camera were combined in the single unit seen at the right in Fig. 2. This entire unit could be rotated as a whole about the reflected beam as an axis, or the analyzer or compensator could be rotated independently, and clamped in any position. The plate holder was arranged so that it could be slid above the shutter opening so as to receive ten pictures on a single plate.

The type of compensator employed deserves special mention. It consisted of a thin glass plate (a microscope cover slide) selected for freedom from initial strain. Such a glass is isotropic and light travels through it with the same speed in all directions. However, when this glass is strained by tension it becomes doubly refracting like a positive uniaxial crystal with the optic axis in the direction of strain. Within the limits to which Hooke's law applies it has been found[5] that for a given thickness of glass, the amount of double refraction as measured by the relative retardation of the polarized light components parallel and perpendicular to the direction of strain is directly proportional to the stress applied. On this basis, the thin glass plate was mounted so that controlled tension could be applied in order to impose known retardations upon the components of a transmitted beam. Actually two such plates were used at right angles to each other. Strain in one offsets the effects on polarization of strain in the other. The strains required for mutual neutralization being known, ellipticity in the transmitted beam was revealed and measured by a departure from the neutralization set-

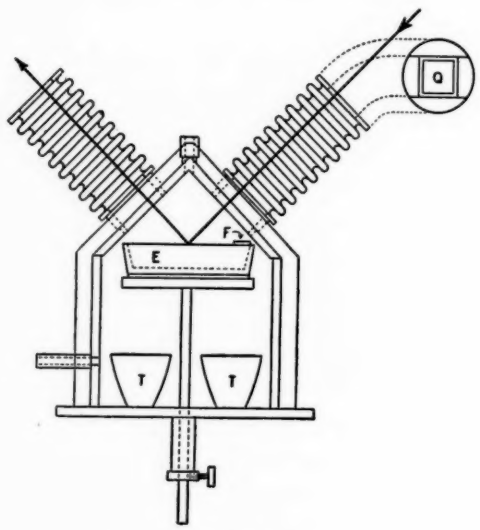

FIG. 3.

[5] Coker and Filon, *Photoelasticity*.

ting which had been found with truly plane polarized light.

Details of the compensator are shown in Fig. 4. *A*, *A*, are nuts bearing the screws, *C*, *C*, which serve to determine the extent to which the strong strings *B*, *B*, are stretched. *D*, *D*, are triangular devices for applying a uniform strain to the compensator plates which overlap at *K*. When in use the entire front of the compensator is covered with black paper, with a square hole immediately in front of *K* only to insure that all light pass through the compensator.

Calibration and Adjustments

The strain-glass compensators were calibrated for Δ *versus* strain against a Berek[6] compensator between crossed Nicols in a polarization microscope. On the stage of the microscope was cemented a "Rot I Gyps" crystal with its axis at a very slight angle to the plane of polarization so that there would be not quite complete extinction of the field of view. Then with the Berek, the phase differences were measured under three conditions, (1) with the compensator glass under a known number of divisions of strain on the stage, (2) with the compensator glass under zero strain on the stage. and (3) without the compensator on the stage. Settings were made on the grayish-violet "teinte sensible" between the red and blue with great precision. For each of many degrees of strain, 50 to 100 readings of the retardation were recorded in order to enhance the accuracy of the mean result. In this way well-defined and accurately located straight line Δ-strain calibration curves were plotted for each compensating strain-glass.

In the theory presented above, Drude's equations involve λ, the wave-length. In view of the very low intensity of the light reflected from an aqueous medium and transmitted through the crossed analyzer the monochromaticity demanded by theory was sacrificed for intensity. Accordingly, all wave-lengths from a rather intense mercury arc were utilized. The disadvantage of this is that all wave-lengths are not compensated simultaneously.

The weighted mean or dominant wave-length was estimated in the following manner. With the polarizer set at a large azimuth, α, measured from the horizontal, the angle of incidence was varied until the reflected ellipse had its major axis exactly horizontal, as determined photographically through the analyzing Nicol with axis set to intercept horizontal vibrations. When the major axis is horizontal, the angle of indidence is the polarizing angle. The tangent of this angle is the refractive index of the reflecting

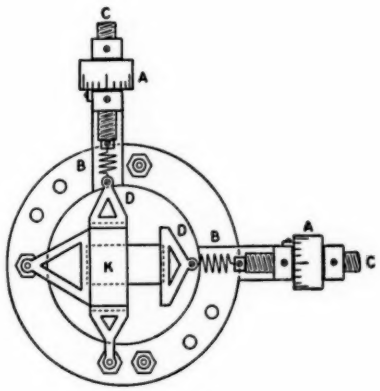

Fig. 4.

liquid. By using dispersion data from the *International Critical Tables* in Cauchy's formula $\mu_2 = A + B/\lambda^2$, the wave-length corresponding to this value of the refractive index was calculated. The advantage of this procedure lies in the high rate of change of tilt of the major axis with angle of incidence when α is large.

The angle of incidence was read to 1 minute of arc by means of graduated scale and vernier, after careful calibration of the scale itself and attention to the exact scale reading at which the slits were vertical.

The zero azimuth of the scale of the analyzer was obtained by viewing through the analyzer a beam of horizontally plane polarized light reflected from a clean mercury surface. The azimuth of the analyzer was varied until the image could be almost completely extinguished. The zero azimuth of the polarizer was determined by crossing with the analyzer while the two were straight in line.

Before using the paraffined boat which served as the container for the experimental liquid, it was washed in a slow stream of distilled water for

[6] M. Berek, Zentralbl. f. Min. 388, 427, 464, 580 (1913). Ernst Leitz, *Gebrauchsanweisung und Tabelle zum Kompensator nach Berek.*

TABLE I. *Data of H. D. Bruce for pure water, at 20.0°C.* $\lambda=5114A$, $\mu_2=1.3359$, $\alpha=99°\ 03'$, *polarizing angle* $=53°\ 11'$, $\gamma=135°$.

ANGLE OF INCIDENCE	Δc OBSERVED	TAN Δ	D
53° 11′	$-6.6\times10^{-4}\lambda$	∞	−0.253
51° 34′	−7.1	−0.00710	−0.291
50° 11′	−9.0	− .00371	−0.249
49° 51′	−9.9	− .00335	−0.253
49° 15′	−12.5	− .00285	−0.253
48° 50′	−14.9	− .00241	−0.238
48° 32′	−20.1	− .00238	−0.254
48° 29′	−21.0	− .00234	−0.253
		Average	−0.256

several days in order to remove any trace of soluble or surface spreading impurity. This vessel was always filled to brimming capacity with conductivity water then repeatedly swept with pulp paper strips to reduce the water to a constant level and to render the surface clean. In the case of our experiments with water, this sweeping was performed between each exposure.

The experiment proper consisted of taking a number of exposures each of the same time interval but varying the strain setting of one of the compensator glasses between exposures. A series of 9 or 10 pictures were taken on one plate. These several pictures were then studied to locate the one of minimum darkening. Whenever doubtful, the position of the minimum darkening was determined by means of a recording microphotometer. The picture of minimum darkening represents the condition of most nearly exact compensation of the reflected ellipse and extinction by the analyzer. For this picture, the setting of the dials of the two strain plates will not be quite the same as they were for mutual compensation in the absence of the reflecting surface. The difference gives the value for the phase difference of the reflected ellipse.

EXPERIMENTAL RESULTS

In Tables I and II for pure water, Δc, observed with the strain-glass compensator plate, is the retardation along the compensator axes of the perpendicular component of the reflected polarized light behind the parallel component. Tan Δ is calculated from Δc by the following equation

$$\tan\Delta=\frac{\sin 2(\phi-\gamma)}{\sin 2\phi}\tan\Delta c, \qquad (5)$$

where γ is the azimuth of the compensator axis, and ϕ, the azimuth of the major axis of the ellipse which for purposes of calculation is practically equal to β of the Fresnel formula

$$\tan\beta=-\tan\alpha\frac{\cos(i+r)}{\cos(i-r)}. \qquad (6)$$

The significance of the Drude constant, D, in the last column of Tables I and II, is

$$D=\tan\Delta\Big/\left(\frac{4\pi}{\lambda}\,\frac{\mu_2^2/\mu_1}{\mu_1^2-\mu_2^2}\,\frac{\sin i\tan i}{\tan^2 i-\mu_2^2/\mu_1^2}\right). \qquad (7)$$

According to Drude's theory in Eqs. (1) and (2), D should be a constant; namely,

$$D=\int_0^l\frac{(\mu^2-\mu_1^2)(\mu^2-\mu_2^2)}{\mu^2}dz. \qquad (8)$$

The value for D at the polarizing angle was calculated by substituting Eqs. (4) and (8) into Drude's Eq. (2) to get Eq. (9).

$$\frac{\tan 45°}{\tan\alpha}\tan\frac{\Delta c}{2}=\frac{\pi}{\lambda}\,\frac{(\mu_1^2+\mu_2^2)^{\frac{1}{2}}}{\mu_1^2-\mu_2^2}D. \qquad (9)$$

Bacon did this work in 1932, Bruce in 1938. In the intervening time the necessity for extreme accuracy in determining the polarizing angle was more keenly realized and in the latter work improvement was made in this regard. Nevertheless, it must be admitted that the reliability of both results suffer from lack of very definite knowledge of the wave-length of the light, a defect which can now be overcome by use of the Bol light and monochromatic filters.

The observational error in Δc is about the error of one strain graduation, $1.2\times10^{-4}\lambda$, or about 0.6A. The concomitant error in D is ±0.05 at the polarizing angle but only ±0.015 five degrees away.

TABLE II. *Data of R. C. Bacon for pure water, at 20.0°C.* $\lambda=5560$A, $\mu_2=1.3335$, $\alpha=82°\ 36'$, *polarizing angle* $=53°\ 8'$, $\gamma=135°$.

ANGLE OF INCIDENCE	Δc OBSERVED	TAN Δ	D
53° 8′	$10.2\times10^{-4}\lambda$	∞	−0.3475

Since μ, the refractive index of the surface film of water, is not known, l cannot be directly calculated from the value of D as measured. However, by assuming constant values for μ, corresponding values for l can be estimated. This has been done in Table III.

The value 2.26A is the least possible thickness, compatible with our observations and Drude's theory, which the surface film could have. From x-ray data Burton and Oliver[7] have given 3.7A as the molecular spacing of amorphous vitreous ice and Bernal[8] gives 2.76A as the shortest molecular distance in water. Accordingly, our observations indicate that the thickness of the surface of pure water is of a molecular order of magnitude and may be no more than the outermost layer of molecules.

For light polarized at 45° azimuth incident on water at the polarizing angle, the ellipticity of the reflected beam has been measured by Lord Rayleigh,[9] Raman and Ramdas,[10] and Bouhet.[11] Our observational data permit us also to calculate this ellipticity by means of the relation $\tilde{\rho}=\tan \Delta/2=\Delta/2$. The several results are given in Table IV.

TABLE III.

ASSUMED VALUE FOR THE INDEX OF THE SURFACE	SURFACE THICKNESS, OF PURE WATER $D=-0.256$	$D=-0.347$
1.0000, the index for air	∞ A	∞ A
1.1558, $(\mu_1\mu_2)^{\frac{1}{2}}$	2.26	3.07
1.2691, 0.95×1.3359	3.87	5.25
1.310, the index for ice	8.94	12.13
1.3191, $1.0+0.95(1.3359-1.0)$	13.47	18.28
1.3359, the index for water	∞	∞

TABLE IV.

OBSERVER	ELLIPTICITY FROM WATER AT THE POLARIZING ANGLE
Rayleigh	0.00042
Raman and Ramdas	0.00075
Bouhet	0.00040
Bacon	0.00042
Bruce	0.00033

In comparing results for a pure liquid one may bear in mind that the more rigorous the sweeping of the surface the lower the ellipticity should be. Likewise the accuracy in the neighborhood of the polarizing angle is increased by every improvement in the method of measuring the angle of incidence.

It is planned to extend the experimental procedure described in this paper to a study of salt and soap solutions and to surface active oil films.

The authors likewise wish to call attention to the ingenious photometrical method of Frazer for studying surface films.[12]

[7] Burton and Oliver, Nature **135**, 505 (1935).
[8] Bernal, Nature **132**, 993 (1933).
[9] Rayleigh, Phil. Mag. (6) **23**, 431 (1912); (6) **16**, 444 (1908); (5) **33**, 1 (1892).
[10] Raman and Ramdas, Phil. Mag. (7) **3**, 220 (1927).
[11] Bouhet, Comptes rendus **185**, 53, 200 (1927); Ann. de physique (10) **15**, 5 (1931).
[12] Frazer, Phys. Rev. **33**, 97 (1929); Phys. Rev. **34**, 644 (1929); Adams, Phys. Rev. **34**, 1438 (1929); Silverman, Phys. Rev. **36**, 311 (1930).

Ions of Europium Distributed Between Different Configurations in Homogeneous Solutions

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Changes in the environment of europium ions in solution bring about changes in the structure of the absorption spectrum. For example, an aqueous solution of europium chloride upon having potassium nitrate added to it gives rise to the structures in the spectra of europium nitrate, in addition to the spectrum of europium chloride. Structures in the spectra of europium salts in alcohol differ from those in water. In a mixed solvent of water and alcohol both spectra are present with relative intensities which vary according to the relative amounts of the components. Europium chloride in the mixed solvent has a spectrum which cannot be distinguished from the exact superposition of the spectra of europium chloride in pure water and in pure alcohol. However, the spectrum of europium nitrate in the mixed solvent has its lines shifted from the positions they occupy in the spectra of the nitrate in the pure solvents. The shifts seem to vary continuously with the proportions of water to alcohol. Nevertheless, the lines remain sharp as successive amounts of water are added, with no suggestion that the lines are a blur, between the spectra of the limiting concentrations. The implications of these results are briefly discussed in their bearing upon the behavior of electrolytes in mixed solvents.

THE salts of europium in solution are not alike in the detailed structures of their absorption spectra and a particular salt gives rise to different spectra when it is dissolved in different solvents. In many instances, structures in the spectra can be resolved into lines, the numbers of which have been interpreted as representing the symmetry of the electrical fields about the europium ions.[1, 2] According to theory, a line in the spectrum of an ion in an electrical field is generally decomposed into a group of lines by fields of lower symmetry. Bethe[3] has derived the numbers of components into which a particular energy level will be decomposed. That the groups of lines in the spectra may be ascribed to this origin is supported by the facts, (a) salts of europium are strongly dissociated electrolytes.[4] The magnetic susceptibilities also show that trivalent europium is ionic in its salts,[5, 6] with ^7F for its basic state; (b) when ions of a rare earth are present in crystals of different symmetry, the structures in the spectra differ in the same way as those of the different solutions of europium.

We shall as in previous publications confine the discussion mainly to europium chloride and europium nitrate since they illustrate the phenomena we are to consider, deferring to later communications the behavior of other salts. The salts of europium were prepared from the oxalate kindly furnished us in a very pure state by Dr. H. N. McCoy. We wish to acknowledge here our great indebtedness to him.

In this communication we shall consider solutions which give rise to several spectra at the same time. Such solutions consist of a salt of europium dissolved in a homogeneous liquid phase of two components. An instance is already known where two absorption spectra appear when the solvent consists of only one component —europium nitrate dissolved in water. The relative intensities of these spectra vary with the concentration. The group in the spectrum at about 4650A consists of a triplet in the range of concentrations from about 1.5 M to 0.01 M. This triplet shall be referred to as the nitrate-triplet. On further dilution an additional spectrum makes its appearance, with a quartet as its structure at about 4650A and it gains in relative intensity as dilution proceeds. At 0.0007 M there is scarcely a trace left of the nitrate-triplet. This quartet we shall call the chloride-quartet because it occurs in the spectrum of europium chloride in aqueous solution, remaining practically unaffected by dilution in the range investigated—1.5 M to 0.0007 M.

[1] S. Freed and S. I. Weissman, J. Chem. Phys. **6**, 297 (1938).
[2] S. Freed and H. F. Jacobson, J. Chem. Phys. **6**, 654 (1938).
[3] H. Bethe, Ann. d. Physik **3**, 133 (1929).
[4] I. M. Klotz, J. Chem. Phys. **6**, 907 (1938).
[5] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford, 1932), pp. 243, 246.
[6] H. Decker, Ann. d. Physik **79**, 324 (1926).

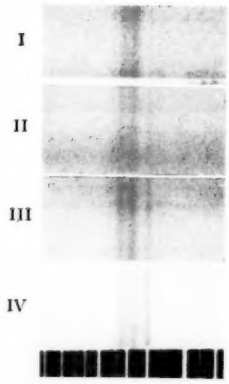

FIG. 1. Solution of 0.003 mole europium chloride in 150 cc water to which was added, I, 0.25 g KNO_3; II, 0.50 g KNO_3; III, 0.78 g KNO_3; IV, pure europium nitrate in water.

When a little potassium nitrate was added to an aqueous solution of europium chloride, besides the chloride-quartet of the latter, the nitrate-triplet appeared, unaccompanied by any other structures in the group at 4650A (see Fig. 1). The intensity of the nitrate-triplet seemed no greater than that which originates from a solution of europium nitrate containing the same concentration of nitrate as was furnished by the potassium nitrate. Hence no definite assertion can be made that the chloride ions cooperate with the nitrate ions in producing the nitrate-triplet. When the nitrate ion concentration was increased until it equaled that of the chloride ion, the chloride-quartet seemed almost entirely suppressed.

When anhydrous europium nitrate was dissolved in anhydrous ether, two strong lines occupied the place of the nitrate-triplet.[1] The question naturally arose—what modifications would occur in the spectrum when water is added

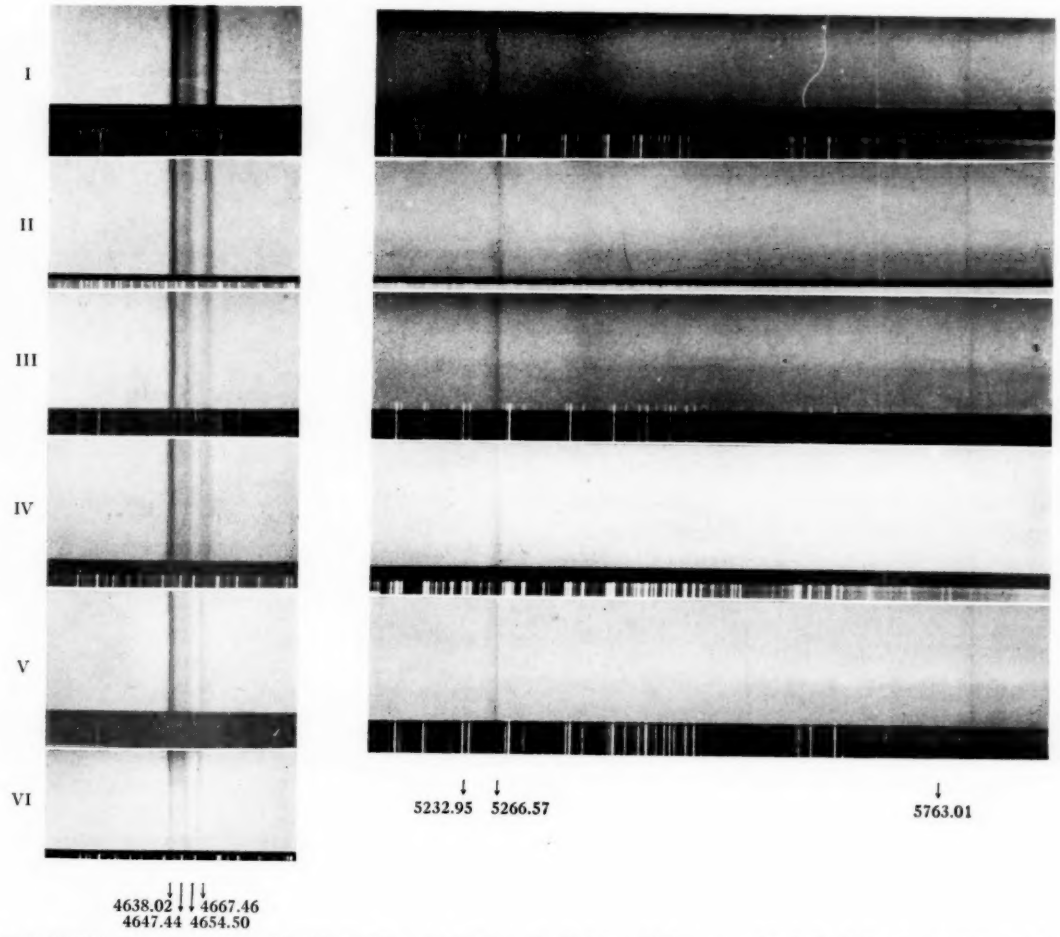

FIG. 2. 0.0012 mole europium chloride in 60 cc anhydrous alcohol to which were added the following amounts of water; I, 0.0 cc; II, 0.16 cc; III, 0.30 cc; IV, 0.45 cc; V, 0.62 cc; VI, solution contains 10 percent water.

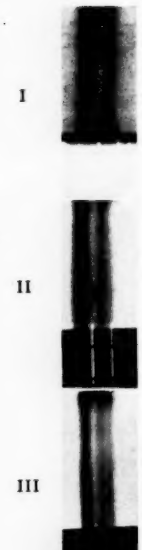

FIG. 3. Concentrated solution of europium nitrate (0.001 mole) in 60 cc anhydrous alcohol to which the following amounts of water were added; I, 0.0 cc; II, 0.87 cc; III, 4.03 cc; IV, 10.06 cc; V, 19.88 cc.

little by little to the solution of the nitrate in ether? It was in response to the same sort of question that potassium nitrate was added to a solution of europium chloride. The situations we are to describe consist of anhydrous europium chloride in absolute alcohol to which water is added in increasing portions and anhydrous europium nitrate in the same mixed solvent.

Anhydrous europium chloride was prepared under conditions suggested by Dr. G. P. Baxter of Harvard University. The hexahydrate was heated in a stream of dry hydrogen chloride between 130°C and 140°C. The released water vapor which condensed on the cooler parts of the glass apparatus was pumped out of the system after the temperature of the furnace had been lowered to room temperature. A stream of dry hydrogen chloride was then passed over the salt again and the temperature was raised back to 130°C–140°C. This cycle was repeated until no further mist could be seen to collect on the glass. According to Dr. Baxter, dehydration carried out at 130°C results in about 0.1 percent or less moisture in the chloride.

The ethyl alcohol used to dissolve the chloride was prepared by dehydrating 95-percent ethyl alcohol over anhydrous calcium sulfate ("drierite").[7] The dried alcohol after distillation had a refractive index n_D^{25} 1.35944 which according to the *International Critical Tables* corresponds to a purity of 99.93 percent±0.06 percent. We never succeeded in obtaining alcohol of this purity again by this method. With magnesium ethylate, however,[8] this purity was easily achieved. Commercial absolute alcohol was refluxed over the magnesium ethylate and then distilled in an all-glass apparatus. Alcohol dried in this way had a refractive index identical with that dried with "drierite" but another attempt led to a refractive index n_D^{25} 1.35939 or a purity of 100.05 percent±0.06 percent according to the values in the *International Critical Tables*.

The dilute europium nitrate solution was made by dissolving 0.077 g europium nitrate in 40 cc of alcohol 99.93 percent pure to which 20 cc of the purest alcohol was added.

The anhydrous europium nitrate was obtained by dehydrating the hexahydrate under two sets of conditions, one recommended by Dr. B. S. Hopkins of the University

FIG. 4. Dilute solution of europium nitrate (0.0012 mole) in 60 cc anhydrous alcohol to which the following amounts of water were added; I, 0.0 cc; II, 0.02 cc; III, 1.01 cc; IV, 10.68 cc; V, 12.88 cc; VI, 15.88 cc.

[7] W. A. Hammond and J. R. Withrow, J. Ind. and Eng. Chem. **25**, 1112 (1933).
[8] H. Lund and J. Bjerrum, Ber. **64B**, 210, (1931).

of Illinois which consisted in heating at 90°C for four days in a vacuum line at a final pressure of about 10^{-5} mm Hg. The other procedure due to Dr. P. Selwood of Northwestern University was to heat the hydrate at 200° to 220°C for about three hours in a high vacuum. First the nitrate was heated for several hours at 130°C. Then the lumps of solid were powdered by grinding with a glass rod. Finally the temperature was raised to 200°C–220°C. It was found in a test that the products resulting from both methods had the same spectra and thereafter the shorter method was employed.

The spectrum of the anhydrous chloride in 99.93-percent alcohol consisted of a triplet in the region 4650A with wave-lengths 4641A; 4650A (rather diffuse) and 4662.5A. This triplet is reproduced in Fig. 2. In the green was a rather fuzzy doublet about 6A wide over-all with center at 5260A, at 5340A a faint diffuse band about 40A wide, and in the yellow two sharp lines very close together, the more intense component at 5795A. To 65 cc of the alcoholic solution which contained 0.28 g $EuCl_3$ 0.09 cc water was added. (The absorption tube was about 90 cm long). A considerable drop in the intensity of the absorption was noted at once and this decrease continued with further additions of water. A faint new line appeared at 4658A. The faint line in the yellow also increased in strength relative to its neighbor. Indeed its strength seemed to come at the expense of the neighboring line. The lines at 4641A and 4650A showed little change in their intensities. The conclusion to be drawn is that these two lines represent the superposition of the lines of the alcoholate and of the hydrate and that the relative sums of the intensities change but little as the transformation of the alcoholate into the hydrate takes place. The isolated lines of these forms at 4658A (hydrate) and 4661A (alcoholate) change a great deal in their intensities. Upon adding more water the line which had been rather diffuse at 4650.0A became sharper and a new line at 4645.5A appeared. When the solution contained about 10 percent water the alcoholate line at 4661A had completely disappeared. The chloride-quartet of the aqueous solution was now unmistakably present alone and further dilution merely confirmed its presence.

Changes in the green and in the yellow regions of the spectrum also accompanied the change in the solvent. New lines set in at 5251A and 5255A besides the strong line at 5258A. In 99.93-percent alcohol the rather fuzzy structure had appeared on the long wave-length side of the stronger line. The faint line in the yellow region became stronger with increased amounts of water and its companion weaker. Finally the latter disappeared. The presence of the original faint line in the alcohol spectrum must be ascribed to the water still present in the alcohol. That this inference is correct is confirmed by the absence of this component when the nitrate was dissolved in a dryer alcohol, and its emergence in the spectrum of the nitrate when water was added. In the spectra of the chloride, no perceptible shift occurred in the lines of the spectrum as the nature of the solvent was altered. In a strict sense, the combined spectrum in the alcohol-water mixtures may be taken as the superposition of the spectrum of the chloride in pure alcohol and of the spectrum of the chloride in pure water. Only the relative amounts of the separate forms changed.

The spectrum of europium nitrate showed variation as the composition of the solvent was changed. In 99.96-percent alcohol (a mixture of the two preparations of alcohol previously described) the spectrum at 4650A was made up of three lines having but little resemblance to the nitrate-triplet. The lines of the latter were almost of equal intensity and the intervals were roughly equal. The triplet from alcohol had two of their lines so close together that the group might have been taken for a doublet had not a resolution been obtained from a more dilute solution.[9] In alcohol the salt possessed lines at 4650.3A; 4658.6A; and at 4660.7A. There was a very faint line at 4648.1A which gained in strength when water was added and hence it owed its origin to the water still left in the alcohol. As this line became stronger, the line at 4660.7A became weaker but persisted to a rather high concentration of water. It could no

[9] When the nitrate was dissolved in ether (reference 1) a doublet appeared in this region of the spectrum. We have then the progression—an evenly spaced triplet from water, a triplet with two of the lines close together from alcohol, and a doublet (a fusion of the two lines?) from ether. This behavior is in agreement with the idea that with greater polarity of the solvent, the energy levels of the dissolved ions are decomposed to a greater degree and that in less polar solvents the fields acting upon the dissolved ions are more symmetrical.

longer be detected when the solution contained 20 percent water.

In the green region of the spectrum the lines were rather diffuse and difficult to characterize. In the yellow, only one line occurred in the spectrum of the nitrate in the alcohol. However, a second one appeared next to it immediately as water was added and the strong line originally present weakened and finally disappeared.

As with the chloride, the intensity of the absorption was greatly decreased when dilution with water took place. The spectrum of the nitrate became especially diffuse when about 4.5 cc of water had been added. The lines sharpened however, as the content in water was further increased. Another sign of interaction of the "pure forms" was brought out by the shifting of the lines as dilution progressed. No such behavior had been observed in the spectra of the chloride. However, it was possible, by following the shift as dilution proceeded, to identify the lines by the positions they assumed when the only remaining spectrum was that of the hydrate. This spectrum was present alone when the water composed 25 percent of the solvent.

The movement of the lines can be observed on Fig. 3 and Fig. 4 by comparing with the adjacent emission spectrum of the iron arc. For example, the line of the hydrate which was barely visible in alcohol had a wave-length of 4647.5A but when the solution consisted of 25 percent water the wave-length was 4645.0A. Whether there existed any discontinuities in the shifts of these lines as a function of the amount of water added we are unable to state at present. The shift appeared gradual within the errors of measurement. Nevertheless, the lines remained sharp, not spreading over the intervals through which the lines were displaced. The sharpness of the lines rules out the possibility that they were a blend between their initial and final positions, that is, between the spectra of the salt in absolute alcohol and in pure water.

It has already been observed[10] that the rather diffuse spectra of the salts of neodymium and of praseodymium showed differences when the salts were dissolved in water and in alcohol and that differences persisted in the mixed solvent.

It has become the practice in some experiments involving the inter-ionic attraction theory to synthesize a solvent of a given dielectric constant by mixing various substances. In the light of the spectroscopic results, it is to be observed that the components of the solvent are singled out by the ions and they take part in different configurations of the electrical fields about the ions. To some degree these ions possess different properties. However, if the behavior of europium nitrate is taken as a guide, it would seem that each configuration is affected in a continuous manner as the solvent is gradually changed. That is, a given configuration seems to respond rather sharply to some average in the macroscopic properties of the pure solvents.

This work is greatly indebted to the Penrose Fund of the American Philosophical Society.

[10] H. C. Jones and J. A. Anderson, *The Absorption Spectra of Solutions* (Carnegie Institution of Washington, 1909), pp. 79, 95.

The Viscosity and Molecular Diameter of Azomethane*

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Measurements of the rate of flow of azomethane at low pressures have been interpreted according to Poiseuille's law corrected for slippage to give an average viscosity of 0.754×10^{-4} poise at 23°C. Assuming a Sutherland constant of 362 from the similar compound β-butylene the molecular diameter of azomethane is found to be 4.54A.

IN connection with some work now under way it was necessary to calibrate a flowmeter to measure rates of flow of azomethane. Sufficient data were obtained to calculate the viscosity and the molecular diameter of azomethane, the latter using a reasonable assumption.

Experimental

The azomethane was prepared using the method of Jahn.[1] The azomethane cuprous chloride complex was decomposed by heating in vacuum to about 135–140°C, and the azomethane frozen out by liquid air, after having passed through two soda-lime columns separated by a toluene-solid CO_2 trap. The azomethane so prepared was distilled back and forth in the system from solid CO_2 to liquid air ten times, discarding the very first and last fractions each time. The resultant product had a vapor pressure of 751 mm at 0°C and a pressure of 7.2 mm at −78°C.

During the runs the azomethane was kept in a reservoir cooled with toluene-solid CO_2. The pressure of the outgoing vapor was regulated by controlling a stopcock above the reservoir. Runs were carried out for only fifteen minutes to conserve the azomethane. The flowmeter was of the usual type, consisting of a capillary tube between two McLeod gauges. The length of the capillary was 69.7 mm and its internal diameter 1.40 mm, as determined by weighing a column of mercury in the capillary. The McLeod gauges used were capable of being read accurately to 0.01 mm. The distance from the reservoir to the capillary was 75 cm, long enough to enable the azomethane to attain room temperature before reaching the capillary.

After passing through the capillary the azomethane was frozen out in a liquid-air trap placed before the mercury and Hyvac pumps used to exhaust the system. At the end of each run the liquid air was removed and the azomethane forced over to a gas burette by means of a Toepler pump and the volume of gas measured over mercury. All volumes were reduced to standard temperature and pressure.

It was found that unless the azomethane reservoir was tapped to cause agitation of the liquid the pressure dropped, probably on account of a lowering of the surface temperature of the liquid and a not sufficiently rapid establishment of thermal equilibrium. When this was done, however, pressures could be kept constant to 0.01–0.02 mm. Once this was established, only two readings were taken over each fifteen-minute interval so as not to disturb the rate of flow. If they checked, the run was used; if not, it was discarded. In this way the results given below were obtained.

Discussion of Results

The viscosity of a gas may be obtained from Poiseuille's law in the form:

$$\frac{\Delta n}{\Delta t}=\frac{d^2\pi}{128L\eta}\cdot\frac{1}{RT}\cdot\frac{(p_2^2-p_1^2)}{2},$$

when Δn is the amount of gas (in moles) passing in time Δt through a capillary of length, L, and diameter, d, with a viscosity, η, under a difference of pressure, p_2-p_1; at the temperature, T. This equation is valid if the flow is viscous and isothermal and if the gas is ideal. These conditions

* Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University, 1939.

[1] Jahn, J. Am. Chem. Soc. **59**, 1761 (1937).

TABLE I.

No.	p_2 MM	p_1 MM	$p_2^2-p_1^2$	V CC	$\eta_a\times10^4$ POISES	$\eta_c\times10^4$ POISES
1	1.88	0.65	3.10	41.2	0.710	0.753
2	1.12	0.41	1.09	14.7	0.696	0.754
3	1.91	0.76	3.09	38.6	0.724	0.762
4	1.79	0.68	2.74	36.1	0.710	0.748
5	1.94	0.74	3.22	41.3	0.728	0.766
6	1.51	0.51	2.02	27.2	0.696	0.740
7	1.97	0.55	3.58	46.6	0.738	0.779
8	1.08	0.35	1.04	14.1	0.675	0.741
					Average	0.754

are met by azomethane under the conditions employed. The experimental results are shown in Table I.

All the runs were made at room temperature, which remained constant at 23–24°C. In the calculations the temperature was assumed constant at 296°K. Viscosities calculated from the simple Poiseuille equation give only the apparent viscosity, η_a, which must be corrected for slippage and for the pressure effect due to the mass motion of the gas. At these slow rates of flow the effect due to the kinetic energy of the mass motion may be entirely neglected, but at the low pressures employed the slip factor is appreciable and must be corrected for.

To obtain the true viscosity, the formula must be corrected by use of the equation:

$$\eta_c=\eta_a\left(1+\frac{8z}{d}\right),$$

where η_c is the corrected viscosity, d is the diameter of the capillary and z is given by[3]

$$z=\frac{1.70\eta_a}{(p_1+p_2)}\left(\frac{3RT}{M}\right)^{\frac{1}{2}}.$$

Applying this correction we obtain the values of η_c given in the last column of the table; the average of the eight runs gives a value of $\eta_c=0.754\times10^{-4}$ poise with an average deviation of approximately one percent.

Molecular diameters may be calculated from viscosity data, provided the data are obtained at at least two different temperatures, so as to permit a determination of the Sutherland constant. Since this work was done at one temperature only, it is impossible to obtain directly a value for the Sutherland constant. Since this constant is really a measure of the attractive forces between the molecules, it should have very nearly the same value for azomethane as for any other molecule having a similar structure and a molecular weight not too far from that of azomethane. Such a molecule, for example, would be β-butylene which has a nearly identical molecular weight and whose configuration is also very similar to that of azomethane, the difference being HC=CH in place of N=N. It is to be expected that the force fields surrounding these two molecules should be nearly the same. That the two molecules have similar attractive forces is evidenced by the fact that their boiling points are nearly identical, both boiling at approximately 1°C. The Sutherland constant for β-butylene has been determined by Titani,[4] who gives it as 362. If we take this as the Sutherland constant for azomethane also, we can calculate the molecular diameter, σ, from the kinetic theory equation:[3]

$$\sigma^2=\frac{0.499\rho\bar{c}l_\infty}{(1+C/T)},$$

where ρ=density of the gas, $\bar{c}$=average velocity of molecules at temperature, T, l_∞=mean free path on basis of nonattracting spheres, and C=Sutherland's constant.

This gives the molecular diameter as 4.54A. A value very slightly less than that for β-butylene is to be expected. Titani gives the molecular diameter of β-butylene as 4.58A, showing that this value of 4.54A cannot be seriously in error. It is interesting to note that Kassel[5] has used the value 3.98A as the molecular diameter for collisional deactivation in azomethane decomposition; this, of course, need not be the same as the diameter obtained from viscosity measurements.

[3] Chapman, Phil. Trans. **217**, 115 (1917).

[4] Titani, Bull. Chem. Soc. Japan **5**, 98 (1930).

[5] Kassel, *Kinetics of Homogeneous Gas Reactions* (A.C.S. Monograph, 1932), p. 195.

On the Interaction of Two Colloidal Particles, Using the Complete Debye-Hückel Equation

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Making use of the original Debye-Hückel equation in the theory of electrolytes, an approximate method of calculating the mutual electrical energy of two colloidal particles has been developed. Only binary electrolytes (symmetrical type) have been considered. The final expression for the energy is of the form

$$(Q_0^2/Da)\{f_1(R/a, \kappa a)+(Q_0/Da)^2(z\epsilon/kT)^2 g(R/a, \kappa a)\}$$

or

$$\zeta^2 Da(1+\kappa a)^2\{f_1(R/a, \kappa a)+\zeta^2(z\epsilon/kT)^2 G(R/a, \kappa a)\},$$

where Q_0, a and ζ are the charge, radius and electrokinetic potential, respectively, of each particle, R is the mutual separation of the two particles, κ the characteristic quantity in the Debye-Hückel theory, being proportional to the square root of the electrolyte concentration, z-z the valency type of the binary electrolyte, D the dielectric constant of the solution, T the temperature, ϵ the electronic charge and k Boltzmann's constant. Contrary to the opinion held by many, it is shown that for symmetrical electrolytes, the commonly quoted restriction $z\epsilon\zeta/kT \ll 1$ need not be satisfied in order that the approximate Debye-Hückel equation be applicable. Provided the particle radius is not too large, the latter equation leads to fairly satisfactory values for both ζ and the mutual energy at ordinary ζ potentials. The coagulating powers of the 1–1, 2–2 and 3–3 valency types of electrolytes are studied in detail and qualitative agreement with experiment is obtained. It is shown that the stability of a sol is sensitive to changes in the ζ potential and that in comparing the relative precipitation values of the different electrolytes one must be careful of any small change in ζ. The distinction between the monovalent ions which coagulate at high concentrations and high potentials and the other ions which precipitate at lower potentials and smaller concentrations is emphasized. The energy of the two particles at large separations is again negative and there is a minimum in the energy as a function of the particle distance.

1. INTRODUCTION

IN two recent papers,[1] the author developed a method of calculating the mutual electrical energy of two hydrophobic colloidal particles, making use of the approximate Debye-Hückel equation in the theory of electrolytes. Since the ordinary electrokinetic potential is rather high it becomes desirable to investigate the corrections that would be introduced by treating the complete Debye-Hückel equation. Now the rigorous treatment of the latter for two colloidal particles is a much more difficult problem than that of the approximate equation. In addition, there are other factors which have been neglected, for example the hydration effect and the image forces. Consequently we have adopted here an approximate method, so chosen as to yield reasonable accuracy and at the same time not require too much labor.

It has been shown elsewhere[2] that when dealing with the approximate Debye-Hückel equation, linear superposition of the potentials for the separate particles is fairly satisfactory provided the electrolyte concentration or particle radius is not too large. This suggests that we consider the linear superposition of the corresponding potentials associated with the complete equation. In doing so, we shall make use of the well-known solution of Gronwall, La Mer and Sandved[3] for true electrolytes. It has been shown in II that the "fluctuation terms" neglected in the Debye-Hückel equation are not important when dealing with the ionic atmospheres of colloidal particles. Hence it is more justifiable to apply the solution of G. L. S. to colloidal particles than to ordinary ions. In this paper we shall only deal with binary electrolytes (symmetrical type), although our method can be readily modified to be applicable to the nonsymmetrical type.

2. POTENTIAL OF A SINGLE PARTICLE

The potential ψ in the ionic atmospheres surrounding the one or two particles will be as-

[1] S. Levine, Proc. Roy. Soc. London **A170, 145, 165** (1939). We shall have occasion to apply some of the results in these papers which will be referred to as I and II.

[2] S. Levine and G. P. Dube, Trans. Faraday Soc. (in the press).

[3] T. H. Gronwall, V. K. La Mer and K. Sandved, Physik. Zeits. **29**, 358 (1928) (referred to as G.L.S. in the text).

TABLE I.*

τ	$\ll 1$	0.1	0.3	0.5	0.8	1	2	3
$-10^3X_3(\tau)$	$10^3\tau^2/6$	0.6612	1.937	2.283	2.078	1.819	0.8376	0.4224
$10^5X_5(\tau)$	$-10^5\tau^2/360$	−1.035	−1.095	0.1336	0.9994	1.070	0.27	0.15
τ	4	5	6	7	8	9	10	$\gg 1$
$-10^3X_3(\tau)$	0.2384	0.1467	0.09638	0.06660	0.04790	0.03557	0.02713	$\sim\frac{10^3}{24\tau^3}$
$10^5X_5(\tau)$	0.065	0.031	0.016	0.0093	0.0054	0.0033	0.0021	$\sim\frac{3\times10^5}{640\tau^5}$

* The values of $X_3(\tau)$ for $\tau\leq 3$ and of $X_5(\tau)$ for $\tau\leq 1$ have been taken from G.L.S.

sumed to satisfy the original Debye-Hückel equation

$$\nabla^2\psi=\frac{8\pi n\epsilon z}{D}\sinh\frac{z\epsilon\psi}{kT}, \tag{1}$$

which is the form for a binary electrolyte (symmetrical type), ϵ being the electronic charge, z the valency and n the number per cc of positive (or negative) ions, D the dielectric constant of the electrolytic solution, T the temperature and k Boltzmann's constant. The boundary conditions are that ψ vanish at infinity and also satisfy Gauss' theorem

$$-\frac{4\pi Q_0}{D}=\int_{S_1}\left(\frac{\partial\psi}{\partial n}\right)_1 dS_1=\int_{S_2}\left(\frac{\partial\psi}{\partial n}\right)_2 dS_2, \tag{2}$$

where the integrals are taken over the surfaces S_1 and S_2 of the two particles, Q_0 and a are the charge and radius respectively of each particle and $\partial/\partial n$ denotes differentiation normal to the surfaces.

The general solution of (1) for a single ion (particle in our case), as obtained by G. L. S., is too complicated for our requirements, but we shall use their series expansion for the potential ζ of the particle itself, namely

$$\zeta=\alpha_1Q_0+\alpha_3Q_0^3+\alpha_5Q_0^5+\cdots, \tag{3}$$

where

$$\alpha_1=1/Da(1+\tau),\quad \alpha_3=\{1/(Da)^3\}(z\epsilon/kT)^2X_3(\tau),$$
$$\alpha_5=\{1/(Da)^5\}(z\epsilon/kT)^4X_5(\tau)\quad\text{and}\quad \tau=\kappa a,$$

$\kappa=(8\pi n\epsilon^2z^2/DkT)^{\frac{1}{2}}$ being the characteristic quantity in the Debye-Hückel theory and the functions $X_3(\tau)$ and $X_5(\tau)$ having been defined by G. L. S.* For small ζ, (1) may be replaced by the approximate Debye-Hückel equation

$$\nabla^2\psi_D=\kappa^2\psi_D. \tag{1i}$$

For a single particle this has the solution $\psi_D{}^0=\{Q_0e^\tau/D(1+\tau)\}e^{-\kappa r}/r$ where r is the distance from the center of the particle, yielding the expression $\zeta_0=\alpha_1Q_0$, the first term in the series (3) for the ζ potential.

It is convenient to introduce other units for Q_0 and ζ in the following manner. When the radius is $a_0=10^{-6}$ cm. then the charge is of the order of $Q_0'=50\epsilon$ and at ordinary temperatures $kT_0\approx4\times10^{-14}$ erg and $D_0\approx80$. This suggests that we introduce $Z'=(Q_0/Da)/(Q_0'/D_0a_0)=1.6\times10^6Z/Da$ where $Q_0=Z\epsilon$, $z'=(z/kT)kT_0=4\times10^{-14}z/kT$ and finally $X=Z'z'$ and $Y=z'\zeta$. Then (3) becomes

$$Y=\beta_1X+\beta_3X^3+\beta_5X^5+\cdots. \tag{4}$$

where

$$\beta_1=3.00\times10^{-4}/(1+\tau),\quad \beta_3=3.90\times10^{-3}X_3(\tau)$$

and

$$\beta_5=5.07\times10^{-2}X_5(\tau),$$

taking $\epsilon=4.80\times10^{-10}$ e.s.u. The advantage in

* $X_3(\tau)=-\frac{1}{6}\frac{\tau^2}{(1+\tau)^4}\{1-4\tau e^{4\tau}E(4\tau)\}$

$$X_5(\tau)=\frac{\tau^5}{120(1+\tau)^6}\Big\{-\frac{1}{3\tau^3}+\frac{1}{\tau^2}+\frac{14}{\tau}-\frac{10}{1+\tau}$$
$$-24e^{6\tau}E(6\tau)-\frac{80}{1+\tau}e^{4\tau}E(4\tau)$$
$$-80\frac{1-\tau}{1+\tau}e^{8\tau}E^2(4\tau)+80e^{6\tau}\int_\tau^\infty\frac{e^{-2u}}{u}E(4u)du\Big\},$$

where

$$E(\alpha\tau)=\int_\tau^\infty\frac{e^{-\alpha u}}{u}du.$$

using this form will become evident below. In Table I the values of $X_3(\tau)$ and $X_5(\tau)$ are given. Since we used an asymptotic expansion* for $X_5(\tau)$ for $\tau>1$, there may be a small error for $\tau=2$ and 3. However, this shall serve our purpose.

The radius of convergence of the series (3) has been estimated by G.L.S. for true electrolytes and we have applied their method to colloidal particles, the details being given in the appendix. In Table II the approximate values for the radius of convergence $X=X_0$ of (3) as a function of τ are shown together with the corresponding values of $Y=Y_0$. Now for the 1–1, 2–2 and 3–3 valency types of electrolytes $z'=1$, 2 and 3 approximately at ordinary temperatures and hence $\zeta=Y$, $Y/2$ and $Y/3$, respectively. Thus we are able to compute from (4) the (approximate) upper limit of X_0 and Y_0 (ζ_0) for which the series (3) may be used for all three types of electrolytes simultaneously. The values of $Y_0(\zeta_0)$ are shown in Table II, which also includes the contributions to Y_0 from the first three terms of the series (4).

The following conclusions can be drawn from Table II. Although ζ_0 decreases with increasing τ (addition of electrolyte or larger particles), for the 1–1 type it does not fall much below 40 millivolts. Furthermore for $\zeta \leqslant \zeta_0$, the contribution from the second and third terms in the series (3) are small compared with that from the first i.e., the approximate Debye-Hückel equation is fairly satisfactory, at least in computing the ζ potential. This favorable situation no longer exists, however, when we pass to the 2–2 type and especially to the 3–3 type of electrolyte. Here the value of ζ_0 is above the critical (co-

* For $\tau \geqslant 4$ we used the expansion

$$X_3(\tau) \sim \frac{-\tau}{24(1+\tau)^4}\left(1-\frac{1}{2\tau}+\frac{3}{8\tau^2}\cdots\right)$$

and for $\tau \geqslant 6$,

$$X_5(\tau) \sim \frac{3}{640}\frac{\tau}{(1+\tau)^6}\left(1-\frac{7}{3\tau}+\frac{65}{18\tau^2}+\cdots\right).$$

TABLE II. *Properties of series for $Y(\zeta)$ in powers of $X(Q_0)$.*

τ		0.1	0.3	1	3	5	10	$\gg 1$
X_0*		1.6	1.2	1.1	1.9	2.6	4.6	0.4τ
$10^4\beta_1 X_0$		4.366	2.771	1.651	1.426	1.301	1.255	1.201
$-10^4\beta_3 X_0^3$		0.106	0.131	0.094	0.113	0.101	0.103	0.104
$10^4\beta_5 X_0^5$		−0.055	−0.014	0.009	0.019	0.019	0.022	0.024
$10^4 Y_0$, e.s.u.		4.205	2.626	1.566	1.332	1.219	1.174	1.121
ζ_0 in millivolts	1–1 type	140	87.5	52.2	44.4	40.6	39.1	37.4
	2–2 type	70	43.8	26.1	22.2	20.3	19.6	18.7
	3–3 type	46.7	29.2	17.4	14.8	13.8	13.0	12.5
p		0.41	1.03	2.4	5.8	7.1	9.0	~10
ξ		0.052	0.066	0.044	0.041	0.036	0.034	0.032
η		0.44	0.26	0.12	0.087	0.074	0.069	0.063
$-13.0X_0^2 g(2,\tau)$		0.0284	0.0287	0.00748	0.00091	0.000204	0.0000168	$-\frac{0.00041}{\tau^2}$
$f_1(2,\tau)+13.0X_0^2 g(2,\tau)$		0.3484	0.2032	0.06076	0.00913	0.003283	0.0007720	$\frac{0.06209}{\tau^2}$
$\frac{13.0X_0^2 X_3(\tau)(1+\tau)(1+3\tau)}{\tau}$		0.314	0.298	0.229	0.264	0.247	0.254	0.260
$-13.0X_0^2 g^*(2,\tau)$		0.0516	0.0547	0.01832	0.00429	0.001624	0.0004521	$\frac{0.04961}{\tau^2}$

* It was shown by G.L.S. that $X_0 \to \infty$ ($Y_0 \to \infty$) as $\tau \to 0$.

TABLE III. *Properties of series for $X(Q_0)$ in powers of $Y(\zeta)$.*

τ		0.1	0.3	1	3	5	10	$\gg 1$
ζ in millivolts	1–1 type	150	135	120	105	90	90	90
	2–2 type	75	67.5	60	52.5	45	45	45
	3–3 type	50	45	40	35	30	30	30
$10^4 Y$ (e.s.u.)		5.0	4.5	4.0	3.5	3.0	3.0	3.0
Y/β_1		1.832	1.949	2.664	4.664	6.00	10.95	1.00τ
$-(\beta_3/\beta_1^4)Y^3$		0.058	0.242	0.894	2.226	2.46	5.15	0.54τ
$\{(3\beta_3^2-\beta_1\beta_5)/\beta_1^3\}/Y^5$		0.045	0.158	0.042	0.918	0.64	0.92	0.08τ
X		1.935	2.349	3.600	7.808	9.10	17.02	1.62τ
Sum of terms in Y^7, Y^9 and Y^{11} (approx.)		0.039	0.123	0.032	0.482	0.28	0.59	0.06τ*
$X/(Y/\beta_1)$		1.06	1.21	1.35	1.67	1.52	1.56	1.62
$\sinh(z\epsilon\zeta/kT)/(z\epsilon\zeta/kT)$		33.7	20.6	12.7	7.96	5.09	5.09	5.09
$\sinh(z\epsilon\zeta/2kT)/(z\epsilon\zeta/2kT)$		3.34	2.75	2.28	1.92	1.64	1.64	1.64
p		0.36	1.0	1.2	50	80	—†	50
ξ		0.049	0.10	0.11	0.20	0.17	0.17	0.17
η		0.49	0.46	0.42	0.37	0.31	0.31	0.31
$1.44\times10^8 Y^2(1+\tau)^3(\tau-1)X_3(\tau)/2\tau$		0.143	0.145	0	−0.159	−0.165	−0.211	−0.270
$1.44\times10^8 Y^2 G(2,\tau)$		−0.013	−0.018	0.0019	0.0041	0.0018	0.00064	$\frac{0.093}{\tau^2}$
$f_1(2,\tau)+1.44\times10^8 Y^2 G(2,\tau)$		0.363	0.214	0.0701	0.0141	0.00527	0.00143	$\frac{0.156}{\tau^2}$
$1+1.44\times10^8 Y^2 G(2,\tau)/f_1(2,\tau)$		0.96	0.92	1.03	1.41	1.51	1.81	2.49
$-1.44\times10^8 Y^2 G^*(2,\tau)$		0.044	0.087	0.0617	0.0163	0.00577	0.00184	$\frac{0.244}{\tau^2}$

* The values in this row are apparently an upper limit for large τ.
† The value of p for $\tau=10$ was unreliable because $X_3(\tau)$ was only computed to two figures.

agulating) potential only for small τ i.e., small particles or low electrolyte concentrations. Again we observe that the first term in the series (3) is much larger than the others for $\zeta \leqslant \zeta_0$.

Although the series (3) is not suitable for high ζ potentials it is shown in the appendix that the inverse series

$$Q_0=\frac{1}{\alpha_1}\zeta-\frac{\alpha_3}{\alpha_1^4}\zeta^3+\frac{1}{\alpha_1^7}(3\alpha_3^2-\alpha_5\alpha_1)\zeta^5+\cdots \quad (3i)$$

converges for all finite values of ζ. The corresponding inverse form to (4) is

$$X=\frac{1}{\beta_1}Y-\frac{\beta_3}{\beta_1^4}Y^3+\frac{1}{\beta_1^7}(3\beta_3^2-\beta_5\beta_1)Y^5+\cdots. \quad (4i)$$

Using (4i) we have chosen convenient values of $Y(\zeta)$ for the 3–3 type (2ζ and 3ζ for 2–2 and 1–1 types, respectively) and have computed the contributions to X from the first three terms in (4i), the results being shown in Table III. Again it is found that the first term forms the major contribution, i.e., (1i) is not too unsatisfactory at the ordinary ζ potentials occurring in experiments. We have estimated the contribution from the next three terms in (4i) (involving the

powers Y^7, Y^9 and Y^{11} in (4i)) and the results, shown in Table III, indicate that they are not important (see Appendix for details).

Now the results obtained here are in disagreement with the common opinion that (1i) can only be used for small ζ potentials. In Table III we have computed the two ratios $\sinh(z\epsilon\zeta/kT)/(z\epsilon\zeta/kT)$ and $X/(Y/\beta_1)=Q_0/Da(1+\tau)\zeta$ both of which are assumed to be equal to unity in the approximate Debye-Hückel theory. It is observed that although the first ratio is considerably larger than unity the same is not true of the second. However, the argument commonly put forward to explain the inadequacy of the approximate Debye-Hückel equation is precisely this large deviation of the first ratio from unity.

An attempt to explain this apparent inconsistency by examining the solution of G.L.S. is given in the appendix. The following remarks will help to clarify the argument. The assumption that is really made when (1i) is used is that $\sinh(z\epsilon\psi_0(r)/kT)/(z\epsilon\psi_0(r)/kT)=1$ where $\psi_0(r)$ drops from ζ to 0 as r increases from a to ∞. Here $\psi_0(r)$ is the general solution of (1) for a single particle, so that $\zeta=\psi_0(a)$. This means that we are taking as unity some kind of average of this ratio over the whole region of the ionic atmosphere ($a\leqslant r\leqslant\infty$). Apparently, this is a far less drastic approximation than taking its (maximum) value at $r=a$ to be unity.[4] Furthermore, according to Table III, the approximate equation is satisfactory even for very high ζ potentials when τ is small. In this case the diffuse layer extends to distances much larger than the particle radius and these outer regions (where (1i) is valid) play an important role in determining the nature of the potential function.

As a further illustration, we shall quote the well-known solution of (1) for a plane surface of charge density σ,

$$\sigma=\frac{DkT\kappa}{2\pi\epsilon}\sinh\frac{\epsilon\zeta}{2kT},$$

reducing to $\sigma_0=D\zeta\kappa/4\pi$ in the approximate solution. The ratio σ/σ_0 has been computed in Table III and we observe that it only deviates strongly from unity for somewhat high ζ potentials. It is also noticed that $X/(Y/\beta_1)\rightarrow\sigma/\sigma_0$ for large τ which is to be expected, since our spherical particle becomes a plane surface for infinite radius (or $\tau=\infty$).

Of course, the above conclusions are confined to binary electrolytes and will probably not hold for the unsymmetrical cases. Thus, Müller[5] found considerable deviations from the approximate Debye-Hückel solution for electrolytes of the type $p-1$ ($p>1$) by solving the complete Debye-Hückel equation graphically. However the values for the potential which he obtained for the 1–1 valency type confirm our contention concerning the applicability of the approximate Debye-Hückel equation.

3. Energy Associated with a Single Particle

In order to calculate the energy associated with a single particle, it is convenient to obtain an approximate solution ψ_0 of (1) which is simple and yet reasonably accurate and which at the same time reduces to the form (3) or (3i) at the surface of the particle. Such a solution is suggested in the following manner.

For a spherical particle, it has been shown by the author[6] that upper and lower limits for ψ_0 are given by

$$\frac{1}{\beta r}\tanh^{-1}Ce^{-\kappa r}<\psi_0<Ae^{-\kappa r}/r, \tag{5}$$

where

$$\beta=z\epsilon/4akT,\quad A=\zeta ae^{\tau}$$

and

$$C=e^{\tau}\tanh(z\epsilon\zeta/4kT).$$

This suggests that a good approximation to ψ_0 is

$$\psi_0{}^*=\frac{1}{(1+p)r}\left[Ae^{-\kappa r}+\frac{p}{\beta}\tanh^{-1}Ce^{-\kappa r}\right], \tag{6}$$

where p is chosen to satify the boundary condition (2) which for a single particle reduces to

$$\left(\frac{\partial\psi_0}{\partial r}\right)_{r=a}=-\frac{Q_0}{Da^2}, \tag{7}$$

[4] Cf. G. S. Hartley, Trans. Faraday Soc. **35**, 31 (1935).

[5] H. Müller (Kolloid Beihefte, **26**, 257 (1928)) obtained the following results for $a=1.58\times10^{-6}$ cm. and $Q_0=86\epsilon$ (1–1 type),

$1/\tau(=y)$	5.5	11.5	4.1	2.18	1.79
ζ (millivolts)	79.5	87.3	74.3	62.5	58
$X/(Y/\beta_1)=Q_0/Da(1+\tau)\zeta$	1.04	1.03	1.06	1.08	1.08

[6] S. Levine, Proc. Roy. Soc. London **A146**, 597 (1934).

yielding

$$p=\{\zeta(1+\tau)-Q_0/Da\}/\{Q_0/Da-\zeta - (2kT\tau/z\epsilon)\sinh(z\epsilon\zeta/2kT)\}$$
$$=\{Y(1+\tau)-3.00\times10^{-14}X\}/\{3.00\times10^{-14}X - Y-1.67\times10^{-14}\tau\sinh 6.00\times10^{3}Y\}. \quad (8)$$

The function ψ_0^* also satisfies the necessary condition $\psi_0^*=\zeta$ at $r=a$ and lies between the upper and lower limits defined by (5). If the inverse hyperbolic tangent in (6) is expanded, we obtain

$$\psi_0^*=B_1\frac{e^{-\kappa r}}{r}+B_3\frac{e^{-3\kappa r}}{r}+B_5\frac{e^{-5\kappa r}}{r}+\cdots, \quad (9)$$

where

$$B_1=\frac{1}{(1+p)}\left(A+\frac{pC}{\beta}\right), \quad B_3=\frac{pC^3}{3(1+p)\beta},$$
$$B_5=\tfrac{3}{5}C^2B_3.$$

At $r=a$, (9) may be written as

$$\psi_0^*=B_1\frac{e^{-\tau}}{a}(1+\xi(1+\eta)),$$
$$\xi=\frac{4}{3}\frac{(kT/z\epsilon)pu^3}{\zeta+(4kT/z\epsilon)pu}=\frac{1.11\times10^{-4}pu^3}{Y+3.33\times10^{-4}pu},$$
$$\eta=\tfrac{3}{5}u^2, \quad u=\tanh\frac{z\epsilon\zeta}{4kT}=\tanh 3.00\times10^{3}Y,$$

ξ being the correction from the second term in the expansion and $\xi\eta$ from the third term. The values of ξ and η corresponding to the radius of convergence X_0 of (4) are shown in Table II and those corresponding to the values chosen for Y in (4i) in Table III. It is seen that the third term in (9) is appreciably smaller than the second except for very small τ, where, however, the first term is very much larger than the others. Furthermore, when $r>a$, the first term in (9) rapidly becomes the dominating one and the third term is quite negligible.

Under these circumstances it was thought sufficient to try as solution for a single particle

$$\psi_0=A_1\frac{e^{-\kappa r_1}}{r_1}+A_3\frac{e^{-3\kappa r_1}}{r_1}=\psi_D^0+\psi_C^0, \quad (10)$$

where subscripts D and C imply the Debye term* and correction term, respectively. Now the method of determining A_1 and A_3 is somewhat arbitrary and we shall assume†

$$(\psi_0)_{r=a}=\zeta=A_1\frac{e^{-\tau}}{a}+A_3\frac{e^{-3\tau}}{a} \quad (11)$$

and

$$Q_0/D=A_1e^{-\tau}(1+\tau)+A_3e^{-3\tau}(1+3\tau), \quad (12)$$

the second condition simply being (7). Now we can work in terms of Q_0 by replacing ζ in (11) by its expansion (3) or in terms of ζ by replacing Q_0 in (12) by (3i). However, the first alternative is more direct in the following calculations and we need only substitute (3i) into the final result for the energy to obtain the form valid for high potentials. Using (3), (11) and (12) yield

$$A_1=ae^{\tau}\left\{\alpha_1Q_0+\frac{(1+3\tau)}{2\tau}\alpha_3Q_0^3+\cdots\right\} \quad (13)$$

and

$$A_3=-\frac{a(1+\tau)}{2\tau}e^{3\tau}\alpha_3Q_0^3+\cdots. \quad (14)$$

We shall only retain the first two terms in the series (3) since this will be sufficient in most cases. It is not convenient to introduce the notation of (4) until we have derived the final result for the mutual energy of the two particles.

As has already been explained in I and II, we first wish to evaluate the work of charging the particle and its ionic atmosphere, under the assumption that κ is constant. This is given by

$$F_1=\int_{V_0}dv\int_0^{\rho_0}\psi_0(\rho)d\rho+\int_0^{Q_0}\zeta(Q)dQ, \quad (15)$$

where ρ is the charge density corresponding to the potential $\psi_0(\rho)$, and V_0 is the volume surrounding a single particle (V_0 may be taken as extending to infinity). ρ_0 is the final charge density associated with $Q=Q_0$. Using Poisson's equation

$$\rho=-\frac{D}{4\pi}\nabla^2\psi_0=-\frac{D}{4\pi}(\nabla^2\psi_D^0+\nabla^2\psi_C^0)$$
$$=-\frac{D\kappa^2}{4\pi}(\psi_D^0+9\psi_C^0), \quad (16)$$

* Strictly speaking, this is only true if $A_1=Q_0e\tau/D(1+\tau)$.

† A more accurate method is to minimize the integral of which (1) is the Eulerian differential equation namely $\int_V[\nabla\phi\cdot\nabla\phi+2\kappa^2(\cosh\phi-1)]dv$, $\phi=z\epsilon\psi/kT$.

the last equation following from the particular forms chosen for ψ_D^0 and ψ_C^0. Then

$$\int_0^{\rho_0}\psi_0 d\rho=-\frac{D\kappa^2}{4\pi}\int_0^{\rho_0}(\psi_D^0+\psi_C^0)d(\psi_D^0+9\psi_C^0) \quad (17i)$$

$$=-\frac{D\kappa^2}{4\pi}\left\{\frac{\psi_D^{0^2}+9\psi_C^{0^2}}{2}+9\int_0^{Q_0}\psi_D^0\frac{d\psi_C^0}{dQ}dQ+\int_0^{Q_0}\psi_C^0\frac{d\psi_D^0}{dQ}dQ\right\} \quad (17ii)$$

$$=-\frac{D\kappa^2}{4\pi}\left\{\frac{\psi_D^{0^2}+9\psi_C^{0^2}}{2}+G_0\psi_D^0\psi_C^0\right\}, \quad (17iii)$$

$$G_0=9-\frac{8}{A_1A_3}\int_0^{Q_0}A_3\frac{dA_1}{dQ}dQ.$$

In (17ii) we have transformed from ρ to Q, which is possible since κ is constant and hence ρ is a function of Q only. To obtain G_0, we integrate by parts the third term on the right-hand side of (17ii) and then substitute (10). Introducing (17iii) into (15)

$$\int_{V_0}dv\int_0^{\rho_0}\psi_0 d\rho=-\frac{A_1^2D\kappa}{4}e^{-2\tau}-\frac{3}{4}D\kappa A_3^2e^{-6\tau}-\frac{D\kappa}{4}G_0A_1A_3e^{-4\tau}, \quad (18)$$

remembering that

$$\int_{V_0}dv=4\pi\int_a^\infty r^2dr.$$

The other term in (15) reads

$$\int_0^{Q_0}\zeta(Q)dQ=\frac{Q_0^2}{2Da(1+\tau)}+\frac{\alpha_3Q_0^4}{4}+\cdots. \quad (19)$$

Adding (18) and (19) and substituting (13) and (14) for A_1 and A_3, respectively (the integral in G_0 is readily evaluated) the energy associated with one particle finally becomes

$$F_1=\frac{Q_0^2}{2Da(1+\tau)}\left\{1-\frac{\tau}{2(1+\tau)}\right\}+\frac{\alpha_3Q_0^4}{4}\left(1+\frac{7}{2}-\frac{1+3\tau}{1+\tau}\right)+\cdots. \quad (20)$$

We first note that when the approximate Debye-Hückel equation is used then only the term in Q_0^2 is obtained. Second, the ordinary internal energy differs from (20) by the term in Q_0^4 being

$$U_1=\tfrac{1}{2}Q_0\zeta+\tfrac{1}{2}\int_{V_0}\rho_0\psi_0 dv$$

$$=\frac{Q_0^2}{2Da(1+\tau)}\left\{1-\frac{\tau}{2(1+\tau)}\right\}+\frac{\alpha_3Q_0^4}{2}\left\{1+\frac{5}{2}-\frac{1}{2}\frac{1+3\tau}{1+\tau}\right\}+\cdots, \quad (21)$$

which can be obtained in a similar fashion to F_1.

4. Two Particles. Mutual Energy

Consider two particles O_1 and O_2 at distance R apart and let $r_1=O_1P$ and $r_2=O_2P$ where P is any point in the surrounding electrolyte solution. Then we shall assume that the potential at P is approximately given by

$$\psi=A_1'\left(\frac{e^{-\kappa r_1}}{r_1}+\frac{e^{-\kappa r_2}}{r_2}\right)+A_3'\left(\frac{e^{-3\kappa r_1}}{r_1}+\frac{e^{-3\kappa r_2}}{r_2}\right)=\psi_D+\psi_C, \quad (22)$$

corresponding to the first approximation in II. According to (II. 27) when

$$A_3'=0, \quad A_1'=A_1/(1-\delta_1)$$

where it is easily calculated that $\delta_1\ll 1$. Similarly we may expect that here $A_1'\approx A_1$ and $A_3'\approx A_3$. Now since the term in A_1' forms the main contribution to ψ in (22), it will be sufficient to choose $A_3'=A_3$ and then find A_1' by applying the boundary condition (2).

Before proceeding any further we need to explain the notation that will be introduced for the sake of brevity. The calculation is quite similar to that carried through in II and indeed, because of the similar forms of ψ_D and ψ_C, very little additional work in the evaluation of the integrals is necessary. In II we defined the quantities δ_1, δ_2, μ_1, μ_2 and $\delta_3=\mu_2-\mu_1$, all of which were functions of τ and s where $s=R/a$ measures the distance between the two particles in units

of the radius. For the sake of reference we have given the forms of these quantities in the appendix and shall denote them by $\delta_1(s, \tau)$, $\delta_2(s, \tau)$, $\mu_1(s, \tau)$, $\mu_2(s, \tau)$ and $\delta_3(s, \tau)$, respectively. Now it will be understood that $\delta_1(s, 3\tau)$ is obtained from $\delta_1(s, \tau)$ simply by replacing τ by 3τ. The quantities $\delta_2(s, 3\tau)$, $\mu_1(s, 2\tau)$ and $\delta_3(s, 3\tau)$ will be defined in an analogous fashion.

To evaluate A_1' we substitute (22) into (2) and, adopting the method described in II, obtain

$$Q_0/D = e^{-\tau}(1+\tau)\{1-\delta_1(s, \tau)\}A_1' + e^{-3\tau}(1+3\tau)\{1-\delta_1(s, 3\tau)\}A_3, \tag{24}$$

which corresponds to II (27). After a little manipulation, (24) becomes

$$A_1' = \frac{A_1 + sA_3}{1-\delta_1(s, \tau)}, \quad s = \frac{e^{-2\tau}(1+3\tau)}{(1+\tau)}\delta_1(s, 3\tau). \tag{25}$$

The energy for the two particles corresponding to (15) will be*

$$F_2 = \int_V dv \int_0^\rho \psi d\rho + 2\int_0^{Q_0} \bar{\Psi}(Q) dQ, \tag{26}$$

where the first integral is taken over the volume of the water medium surrounding the two particles and $\bar{\Psi}(Q)$ is the average value of the potential over the surface of each particle. We have already discussed in II the significance of working with $\bar{\Psi}(Q)$. Corresponding to the expression II (28) we find that

$$\bar{\Psi}(Q) = A_1\frac{e^{-\tau}}{a}\left\{\frac{1+\delta_2(s, \tau)}{1-\delta_1(s, \tau)}\right\} + A_3\frac{e^{-\tau}}{a}\left\{\frac{1+\epsilon_2(s, \tau)}{1-\delta_1(s, \tau)}\right\}, \tag{27}$$

where $$\epsilon_2(s, \tau) = \delta_2(s, 3\tau)\{1-\delta_1(s, \tau)\} - \delta_1(s, \tau) + se^{2\tau}\{1+\delta_2(s, \tau)\}.$$

In place of (17iii) we now derive

$$\int_0^\rho \psi d\rho = -\frac{D\kappa^2}{4\pi}\left[\frac{\psi_D{}^2 + 9\psi_C{}^2}{2} + G\psi_C\psi_D\right], \quad G = 9 - \frac{8}{A_1'A_3}\int_0^{Q_0} A_3\frac{dA_1'}{dQ}dQ. \tag{28}$$

Substituting (22) into (28), by symmetry

$$\int_V dv\int_0^\rho \psi d\rho = -\frac{D\kappa^2}{4\pi}\left[A_1'^2\int_V\left(\frac{e^{-2\kappa r_1}}{r_1{}^2} + \frac{e^{-\kappa(r_1+r_2)}}{r_1r_2}\right)dv + 9A_3{}^2\int_V\left(\frac{e^{-6\kappa r_1}}{r_1{}^2} + \frac{e^{-3\kappa(r_1+r_2)}}{r_1r_2}\right)dv\right.$$
$$\left. + 2GA_1'A_3\int_V\left(\frac{e^{-4\kappa r_1}}{r_1{}^2} + \frac{e^{-\kappa(r_1+3r_2)}}{r_1r_2}\right)dv\right. \tag{29i}$$

$$= -\frac{D\kappa^2A_1{}^2}{2}e^{-2\tau}(1+\delta_3(s, \tau)) - \frac{3}{2}D\kappa A_3{}^2e^{-6\tau}(1+\delta_3(s, 3\tau))$$
$$- \frac{D\kappa}{2}GA_1'A_3e^{-4\tau}\{1+\nu(s, \tau)-\mu_1(s, 2\tau)\}. \tag{29ii}$$

There are three types of integrals in (29i) depending on the form of the exponent, namely $n\kappa r_1$ $(n=2, 4, 6)$, $m\kappa(r_1+r_2)(m=1, 3)$, and $\kappa(r_1+3r_2)$. The first two types have already considered in II and hence we are able to give expressions for them without any difficulty. The last type which contributes the new quantity $\nu(s, \tau)$ can be evaluated as follows. The coordinates r_1, r_2 and φ are introduced, φ being the azimuthal angle about the line O_1O_2, the volume element being $dv = (r_1r_2/R)dr_1dr_2d\varphi$.

* In (26), the upper limit ρ in the first integral is the final charge density in the overlapping ionic atmospheres. This should not be confused with ρ in (15).

Integrating with respect to φ,

$$\int_V \frac{e^{-\kappa(r_1+3r_2)}}{r_1 r_2}dv=\frac{2\pi}{R}\left[\left(\int_{R-a}^{R+a}dr_2\int_a^{R+r_2}dr_1+\int_{R+a}^{\infty}dr_2\int_{r_2-R}^{r_2+R}dr_1+\int_a^{R-a}dr_2\int_{R-r_2}^{R+r_2}dr_1\right)e^{-\kappa(r_1+3r_2)}\right] \tag{30i}$$

$$=\frac{\pi}{\kappa}e^{-4\tau}\nu(s,\tau),$$

$$\nu(s,\tau)=(e^{-s\tau}/2s\tau)\{2e^{2\tau}-1-(e^{-2s\tau}/3)(2e^{6\tau}+1)\}.* \tag{30ii}$$

Substituting (13) and (14) into (27) we find that

$$2\int_0^{Q_0}\bar{\Psi}(Q)dQ=\frac{Q_0^2}{Da(1+\tau)}\left\{\frac{1-\delta_2(s,\tau)}{1+\delta_1(s,\tau)}\right\}+\frac{\alpha_3 Q_0^4}{2}\left\{\frac{1+\epsilon_3(s,\tau)}{1-\delta_1(s,\tau)}\right\}, \tag{31}$$

where $\epsilon_3(s,\tau)=\frac{1}{2}[3\delta_2(s,\tau)-\epsilon_2(s,\tau)+(1/\tau)\{\delta_2(s,\tau)-\epsilon_2(s,\tau)\}]$.

On substituting (13) and (14) into (29ii) (again the integration of G is quite simple) and combining with (31), we derive the following expression for (26),

$$F_2=\frac{Q_0^2}{Da(1+\tau)}\left[\frac{1+\delta_2(s,\tau)}{1-\delta_1(s,\tau)}-\frac{\tau}{(1+\tau)}\frac{1+\delta_3(s,\tau)}{(1-\delta_1(s,\tau))^2}\right]+\frac{\alpha_3 Q_0^4}{2}\left[\frac{1+\epsilon_3(s,\tau)}{1-\delta_1(s,\tau)}+\frac{7}{2}\frac{1+\nu(s,\tau)-\mu_1(s,2\tau)}{1-\delta_1(s,\tau)}\right.$$
$$\left.-\left(\frac{1+3\tau}{1+\tau}\right)\frac{\{1+\delta_3(s,\tau)\}\{1-\delta_1(s,3\tau)\}}{\{1-\delta_1(s,\tau)\}^2}\right]. \tag{32}$$

We now subtract the expression to which F_2 reduces when the particles are infinitely separated, namely $2F_1$ and so obtain the required form for the energy of interaction of the two particles

$$F_2-2F_1=\frac{Q_0^2}{Da}f_1(s,\tau)+\frac{Q_0^4}{(Da)^3}\left(\frac{z\epsilon}{kT}\right)^2 g(s,\tau), \tag{33}$$

where

$$f_1(s,\tau)=f_r^{(1)}(s,\tau)+f_a^{(1)}(s,\tau),$$
$$f_r^{(1)}(s,\tau)=\{\delta_1(s,\tau)+\delta_2(s,\tau)\}/\{1-\delta_1(s,\tau)\}(1+\tau), \tag{34}$$
$$f_a^{(1)}(s,\tau)=\frac{\tau}{2(1+\tau)^2}\frac{1}{1-\delta_1(s,\tau)}\left[1-\delta_1(s,\tau)-\frac{1+\delta_3(s,\tau)}{1-\delta_1(s,\tau)}\right]$$

and

$$g(s,\tau)=g_r(s,\tau)+g_a(s,\tau),$$

$$g_r(s,\tau)=\frac{X_3(\tau)}{2\{1-\delta_1(s,\tau)\}}\left[\delta_1(s,\tau)-\frac{(1+\tau)}{2\tau}\delta_2(s,3\tau)\{1-\delta_1(s,\tau)\}\right.$$
$$\left.+\frac{(1+3\tau)}{2\tau}\left\{\delta_2(s,\tau)\{1-\delta_1(s,3\tau)\}-\delta_1(s,3\tau)\right\}\right], \tag{35}$$

$$g_a(s,\tau)=\frac{X_3(\tau)}{2(1-\delta_1(s,\tau))}\left[\left(\frac{1+3\tau}{1+\tau}\right)\left\{1-\delta_1(s,\tau)-\frac{(1+\delta_3(s,\tau))(1-\delta_1(s,3\tau))}{1-\delta_1(s,\tau)}\right\}\right.$$
$$\left.+\frac{7}{2}\{\delta_1(s,\tau)+\nu(s,\tau)-\mu_1(s,2\tau)\}\right].$$

* It is readily verified that $\nu(2,\tau)=\delta_2(2,\tau)+\delta_2(2,3\tau)$.

TABLE IV.

τ	$f_1(2,\tau)$	$-10^3 g_r(2,\tau)$	$10^3 g_a(2,\tau)$	$-10^3 g(2,\tau)$	$10^3 G(2,\tau)$
$\ll 1$	0.5000	$10^3\tau^2/12$	$-10^3(5\tau^2/24)$	$10^3(7\tau^2/24)$	$-10^3\tau^2/8$
0.1	0.3768	0.2651	−0.5894	0.8545	−0.3707
0.3	0.2319	0.5519	−0.9799	1.5317	−0.6149
0.5	0.1540	0.5076	−0.7228	1.2303	−0.3950
0.8	0.09187	0.3794	−0.3524	0.7317	−0.1439
1.0	0.06824	0.2674	−0.2087	0.4760	0.08196
2.0	0.02198	0.07462	−0.05708	0.08033	0.2712
3.0	0.01004	0.02702	0.007525	0.01949	0.2310
4.0	0.005609	0.01189	0.005715	0.006174	0.1779
5.0	0.003487	0.006008	0.003671	0.002327	0.1372
6.0	0.002364	0.003347	0.002351	0.000996	0.1075
7.0	0.001742	0.002008	0.001477	0.0005305	0.08483
8.0	0.001274	0.001276	0.001051	0.0002252	0.07074
9.0	0.0009897	0.0008487	0.0007316	0.0001171	0.05870
10.0	0.0007888	0.0005863	0.0005251	0.0000612	0.04945
$\gg 1$	$\frac{1}{16\tau^2}\left(1+\frac{7}{2\tau}\right)$	$\frac{11\times 10^3}{1152\tau^4}\left(1-\frac{225}{44\tau}\right)$	$\frac{53\times 10^3}{4608\tau^4}\left(1-\frac{413}{53\tau}\right)$	$-\frac{10^3}{512\tau^4}\left(1-\frac{188}{9\tau}\right)$	$\frac{11\times 10^3}{1536\tau^2}\left(1-\frac{122}{33\tau}\right)$

The function $f_1(s,\tau)$ has already been obtained in II and the properties of its positive (repulsive) term and of its negative (attractive) term $f_a^{(1)}(s,\tau)$ have been examined. The form (35) for $g(s,\tau)$ is readily verified if we substitute for $\epsilon_3(s,\tau)$ defined in (31) and then for $\epsilon_2(s,\tau)$ defined in (27). The two terms in $g(s,\tau)$, namely $g_r(s,\tau)$ and $g_a(s,\tau)$ are not always positive and negative, respectively, and their chief significance is that the first is associated with the charge on the particles and the second with that of the ionic atmospheres.

It is convenient to introduce X already defined in §2 and also $H=z'^2(F_2-2F_1)$. Then (35) can be written as

$$H=9.01\times 10^{-8} DaX^2[f_1(s,\tau)+13.0X^2 g(s,\tau)]. \tag{36}$$

This form for H, consisting of the first two terms of its expansion in powers of X (or Q_0) converges only when $X\leqslant X_0$ (Table II). To obtain the expansion in powers of $\zeta(Y)$ which converges for all values of ζ, we need only substitute (3i) into (33), yielding

$$F_2-2F_1=\zeta^2 Da(1+\tau)^2[f_1(s,\tau)+(z\epsilon/kT)^2\zeta^2 G(s,\tau)], \tag{37}$$

where

$$G(s,\tau)=(1+\tau)^2\{g(s,\tau)-2X_3(\tau)(1+\tau)f_1(s,\tau)\}.$$

The corresponding form in powers of Y results on substituting (4i) into (36i),

$$H=Da\,Y^2(1+\tau)^2[f_1(s,\tau)+1.44\times 10^8 Y^2 G(s,\tau)]. \tag{38}$$

The limiting forms of (36) and (38) at contact ($s=2$) for $\tau\ll 1$ and $\tau\gg 1$ can be obtained from the formulae given in Table IV. When $s\gg 2$ (large separation of the particles)

$$f_1(s,\tau)\approx-\frac{\tau}{2(1+\tau)}e^{-\tau(s-2)},\qquad g_r(s,\tau)\approx\frac{X_3(\tau)}{8\tau^2}\left\{\frac{(1+2\tau+5\tau^2)}{(1+\tau)}-(1+\tau)e^{-2\tau}\right\}\frac{e^{-\tau(s-2)}}{s},$$

$$g(s,\tau)\approx g_a(s,\tau)\approx-\frac{(1+3\tau)}{2(1+\tau)}X_3(\tau)e^{-\tau(s-2)},\quad G(s,\tau)\approx-\frac{(1+\tau)^2}{2}X_3(\tau)e^{-\tau(s-2)}$$

and the corresponding forms of (36) and (38) are

$$H=-9.01\times10^{-8}DaX^2\frac{\tau}{2(1+\tau)^2}e^{-\tau(s-2)}\left\{1+\frac{13.0}{\tau}X_3(\tau)(1+\tau)(1+3\tau)X^2\right\}$$

and

$$H=-\frac{DaY^2}{2}\tau e^{-\tau(s-2)}\left\{1+\frac{1.44\times10^8}{2\tau}(1+\tau)^3(\tau-1)X_3(\tau)Y^2\right\},$$

respectively. The values of the second term in the brackets in both forms for H are given in Tables II and III, respectively. It is seen that this term is considerably less than unity at ordinary ζ potentials and hence the energy remains negative at large separations when the complete Debye-Hückel equation is used with binary electrolytes (symmetrical type). Since the energy is positive at contact a minimum in the energy at an intermediate separation must exist. Thus our statement in I that the minimum in the energy is typical of all hydrophobic sols consisting of spherical particles receives further confirmation here. We shall postpone a detailed investigation of the form of $g(s,\tau)$ as a function of s to a further report.

Finally the expression for the internal energy U_2 which reduces to $2U_1$ at infinite separation can again be readily derived. The term in Q_0^2 in U_2 will be the same as that in F_2. The term in Q_0^4 in U_2 can be derived from the corresponding one in F_2, shown in (32), as follows. The factor $\alpha_3Q_0^4/2$ in (32) is replaced by $\alpha_3Q_0^4$, the fraction $7/2$ in the second term in the brackets (the coefficient of Q_0^4) by $5/2$ and the third term in the brackets is multiplied by $\frac{1}{2}$. Further details are given in the Appendix.

5. Numerical Examples and Applications

It has already been explained in I that when the van der Waals (attractive) energy between the two particles is added to the electrical energy, a maximum in the resultant energy expression is obtained at a separation close to contact. This maximum is the controlling factor in the stability properties of the sol. However, the properties of the energy at contact will be similar to those of the maximum and we shall only deal here with the energy functions (36) and (38) at contact.

In Table IV we have given the values of $f_1(2,\tau)$, $g(2,\tau)$ and $G(2,\tau)$ for various τ. (The properties of $f_1(2,\tau)$ have already been investigated to a considerable extent in I and II.) This permits a comparison of the correction to the mutual energy calculated on the basis of the approximate Debye-Hückel equation with the corresponding one to the potential. In Table III the function $f_1(2,\tau)+1.44\times10^8Y^2G(2,\tau)$ which is taken from (38) has been computed for the values of Y used in §2. The ratio $1+1.44\times10^8Y^2G(2,\tau)/f_1(2,\tau)$ is now to be compared with $X/(Y/\beta_1)$ (neglecting the contribution from the term in Y^5 which is small). It is seen that the correction to the energy is of the same order as that to the ζ potential. Now the values of Y chosen are of the right order for the 3–3 type but are rather high for the lower valency types. If we assume the same ζ potential for the 2–2 as for the 3–3 case, then we shall have the value $\frac{2}{3}Y$ for the former. This value will also apply to the 1–1 type if we assume its ζ potential to be twice that for the other two (higher) valencies. In the two cases 1–1 and 2–2, the correction term becomes $1.44\times10^8(2Y/3)^2G(2,\tau)$, being reduced by a factor of 4/9. Thus the approximate Debye-

TABLE V. *Energy at contact for three valency types.*

VALENCY TYPE	γ MOLES PER LITER (APPROX.)	ζ IN MILLIVOLTS		$(F_2^0-2F_1)_{a=2}/Da^*=\zeta^2(1+\tau)^2f_1(2,\tau)$ (ergs/cm $\times 10^9$)					$(F_2-2F_1)_{a=2}/Da^*=\zeta^2(1+\tau)^2\{f_1(2,\tau)+(z_\epsilon/kT)^2\zeta^2C(2,\tau)\}$ (ergs/cm $\times 10^9$)				
$a\times 10^8$ in cm.				1	2	3	4	5	1	2	3	4	5
1–1	5×10^{-2}	45	τ	7	14	21	28	35	7	14	21	28	35
				0.251	0.202	0.180	0.170	0.164	0.290	0.246	0.228	0.219	0.213
	10^{-3}		τ	1	2	3	4	5	1	2	3	4	5
		30		0.273	0.198	0.161	0.139	0.126	0.274	0.201	0.166	0.146	0.133
		25		0.190	0.138	0.112	0.097	0.088					
		27							0.221	0.163	0.134	0.117	0.107
	4×10^{-3}	30	τ	2	4	6	8	10	2	4	6	8	10
				0.198	0.139	0.116	0.103	0.095	0.201	0.146	0.123	0.111	0.104
2–2	10^{-3}	30	τ	2	4	6	8	10	2	4	6	8	10
				0.198	0.139	0.116	0.103	0.095	0.212	0.165	0.146	0.136	0.130
3–3	10^{-4}		τ	1	2	3	4	5	1	2	3	4	5
		30		0.273	0.198	0.161	0.139	0.126	0.277	0.230	0.209	0.197	0.190
		25		0.190	0.138	0.112	0.097	0.088					
		26							0.208	0.167	0.148	0.137	0.130

* These two expressions are, of course, identical with (40) and (41), respectively.

Hückel equation yields fairly reasonable results for the mutual energy of two colloidal particles at the ordinary ζ potentials for both the 1–1 and 2–2 valency types of electrolyte. In the case of the 3–3 type, the correction arising from the use of the complete equation may be larger, especially for large τ. We have also computed the function $f_1(2,\tau)+13.0X_0^2g(2,\tau)$ the results being shown in Table II. It is observed that the correction term (coefficient of X_0^2) is quite small so that for $X\leqslant X_0$, the approximate Debye-Hückel equation is quite satisfactory.

In I we suggested an explanation for the fact that monovalent ions which coagulate at high electrolyte concentrations have a greater critical ζ potential than other ions. Some additional remarks on this question will help to clarify the situation. There are, in general, two types of monovalent ions, taking as the criterion their coagulating power in hydrophobic sols. The first type are usually positive, simple ions (e.g. alkali ions) with a large energy of hydration, small polarizability and small London-van der Waals energy of adsorption on the surface of the colloidal particles. These coagulate at high concentrations and high ζ potentials. The second are mostly complex inorganic ions or organic ions, with a small energy of hydration, large polarizability and large van der Waals energy of adsorption. These coagulate at much lower concentrations and smaller ζ potentials.* This suggests that the former type is very little adsorbed by the colloidal particles whereas the second type is adsorbed thereby reducing the free charge Q_0 and hence the ζ potential. (The same effect is observed if there is an increase in opposite charge with the first type and no change in charge with the second.) The polyvalent ions may be included with the second type of monovalent ions, the extent of their adsorption by the particle increasing with the valency.

* This rule is only qualitative and there are definite exceptions such as hydrochloric acid and sulphuric acid with a number of sols (e.g. platinum). In addition, the simple negative ions (e.g. halide ions) may perhaps be considered as intermediate between the two extremes. The author is indebted to Dr. F. Eirich for helpful discussions on this proposed rule.

Now it is found that the second class of monovalent ions has a critical ζ potential which is roughly equal to that associated with bivalent coagulating ions. As explained in I, if we use the approximate Debye-Hückel equation, this implies that the value of κ at the coagulation point in both cases is the same. Since κ is proportional to $z\sqrt{\gamma}$ where γ is the electrolyte concentration of a binary z–z valency type, this means that the precipitating concentration of electrolyte for the 1–1 and 2–2 valencies, assuming a common critical ζ potential, are in the ratio $1 : \frac{1}{4}$, which is of the right order of magnitude experimentally provided the coagulating ion is not too large (complex). As an illustration, we have chosen $T=18°C$ so that τ is equal to $\tau_1=a\sqrt{\gamma}/3.04\times10^{-8}$ and $\tau_2=2a\sqrt{\gamma}/3.04\times10^{-8}$ for the 1–1 and 2–2 types, respectively. Taking $\gamma=4\times10^{-3}$ mole per liter for the 1–1 case, $\gamma=10^{-3}$ mole/l for the 2–2 case this yields $\tau_1=\tau_2=2.08\times10^{6}a$, which will be simply replaced by $2\times10^{6}a$ since the example is hypothetical (although roughly conforming to experiment). Further, we choose $\zeta=30$ millivolts, the corresponding values of Y being 10^{-4} and 2×10^{-4} (e.s.u.) for the 1–1 and 2–2 types, respectively. Taking a series of values for a we have computed

$$(F_2{}^0-2F_1)_{s=2}/Da=(Y(1+\tau)/z')^2 f_1(2,\tau) \quad (40)$$

for both cases under consideration, the results being shown in Table V. It is obvious that the value of (40) will be the same for the two cases for a given radius.

If we use the complete Debye-Hückel equation then we evaluate in place of (40)

$$(F_2-2F_1)_{s=2}/Da=(Y(1+\tau)/z')^2 \times\{f_1(2,\tau)+1.44\times10^{8}Y^2G(2,\tau)\} \quad (41)$$

for the same a and Y as above. Assuming that the energy at contact has the common value at coagulation we wish to get the same value of (41) for the two types. From the results in Table V it is seen that the energy in the 1–1 case is somewhat less than in the other (2–2 type). This implies that we must choose a smaller τ for the 1–1 type, so that the ratio $1 : \frac{1}{4}$ introduced above must be replaced by a smaller one.

However, it is found that the coagulating concentration of the larger monovalent organic (or complex) ions may be roughly equal to or even less than that of the bivalent ions. In order to illustrate the situation in these cases, for simplicity, we shall take the same electrolyte concentration and ζ potential for the 1–1 and 2–2 types, namely $\gamma=10^{-3}$ mole/l and $\zeta=30$ mv. Here we shall again replace the values of τ, namely $\tau_1=1.04\times10^{6}a$ and $\tau_2=2.08\times10^{6}a$ by $10^{6}a$ and $2\times10^{6}a$, respectively. We have calculated (40) and (41) for these cases (Table V). Comparison of the two types of electrolytes shows that we can obtain the same value of (40) by taking $\zeta=25$ mv instead of 30 mv for the 1–1 electrolyte. In the case of (41) we need to let ζ lie in the range 27–30 mv for the 1–1 electrolyte. This qualitatively conforms to experiment in some cases and suggests that the more easily the complex ion is adsorbed, i.e., the lower the precipitating concentration, the smaller the critical ζ potential.

Now the fact that often the critical ζ potentials are found to be approximately equal when comparing the large monovalent ions with the bivalent ions is not necessarily in disagreement with our results. Firstly, there are two factors that complicate matters by changing the effective value of κ, namely the adsorption of ions on the surface of the particles and the presence of electrolytes before the addition of our coagulating ion. Secondly, since the complex ions may be quite large, they may change slightly the effective radius of our particle on adsorption. Thirdly, it is questionable whether the Debye-Hückel theory, which neglects the van der Waals forces between the ions, can be applied without introducing some error. In general, the larger the ion, the less important do the purely electrical effects become and the specific nature of the ion enters more and more in determining its properties.

There are left to consider the three cases 1–1, 2–2 and 3–3 electrolytes, assuming that the first type precipitates at higher concentrations and ζ potential. At $T=18°C$, $\tau=\tau_3=3a\sqrt{\gamma}/3.04\times10^{-8}$ for the 3–3 type. We shall take $\gamma\approx5\times10^{-2}$, 10^{-3} and 10^{-4} mole/l for the three valencies and $\zeta=45$ mv for the first (1–1) and $\zeta=30$ mv for the other two. (These values roughly conform to experiment at coagulation.) We find that $\tau_1=7.36\times10^{6}a$, $\tau_2=2.08\times10^{6}a$ and $\tau_3=0.987\times10^{6}a$ which values will be replaced by

$\tau_1=7\times10^6a$, $\tau_2=2\times10^6a$ and $\tau_3=10^6a$. The corresponding values of Y are 1.5×10^{-4}, 2×10^{-4} and 3×10^{-4} (e.s.u.), respectively. In Table V, we have computed (40) and (41) for the three types under consideration.

Again we should like that (41) (and (40) approximately) have a common value with all three types for a given particle radius. On first sight, since the 1–1 and 3–3 electrolytes appear to satisfy roughly this requirement, one may conclude that the energy for the 2–2 type should be greater which can be attained by taking smaller values for τ_2. However, this implies that the coagulating powers of the bivalent ion and trivalent ion have a ratio which is greater than $\frac{1}{10}$. Experimentally, the tendency appears to be in the other direction i.e., for a ratio less than $\frac{1}{10}$. Consequently we have interpreted our results differently in the following manner.

For the sake of argument, we shall assume that the 2–2 type yields the correct energy and we wish to investigate how to adjust ζ for the other two valencies so as to obtain the same energy. Firstly the values of τ_1 are quite large and the correction from the distortion of the outer diffuse layers of the particles may be quite considerable. The ζ potential of the 1–1 case may be greater than 45 mv leading to an even greater discrepancy between the 1–1 and 2–2 electrolytes. To obtain the same energy for these two types, it appears that the polarization terms may reduce the energy by as much as a factor of $\frac{1}{2}$. Secondly the effective value of κ in both cases may be changed by the two factors mentioned above and thirdly the energy at the maximum and not at contact controls coagulation and the properties of the former may be somewhat different.

There is another interpretation of the discrepancy between the 1–1 and 2–2 types which must not be overlooked, namely that the Smoluchowski formula for the cataphoretic velocity U is not correct and hence the values of ζ which have been used here (based on this formula) are subject to some error. Thus, Henry[7] showed that, if the relaxation effect is neglected and the approximate Debye-Hückel equation is used, then ζ is given by $\zeta=4\pi U\eta/DEf(\tau)$ where E is the applied field strength, η is the viscosity of the medium and $f(\tau)$ is a certain function of τ, increasing from $\frac{2}{3}$ to 1 as τ goes from 0 to ∞. Making use of this relation it has been estimated that if the value of ζ is correct for the 2–2 type, then we should take $0.8\zeta^2$ approximately (0.75–0.80) for the 1–1 type, and hence also multiply the energy by 0.8 in the latter case. This correction would bring the energy for the 1–1 and 2–2 types closer together.

Comparison of the 2–2 and 3–3 types shows that we roughly obtain the same value of (40) by choosing $\zeta=30$ mv for the first and $\zeta=25$ mv for the second. The corresponding potentials when calculating (41) are 30 mv and 26 mv, respectively. This suggests that the critical ζ potential is somewhat greater in the former case. Evidence for this is rather lacking since very few experiments with 3–3 electrolytes have been done. However, there are cases where this is true for 2–1 and 3–1 types. When comparing these bivalent ions with the trivalent ones, it must be remembered that particularly for the latter, the effective value of κ may be quite different from that calculated on the basis of the concentration of the added electrolyte. The existence of such a change in κ is clearly illustrated by the dependence of the concentration of the ion on the sol concentration. If we again introduce the correction for ζ, derived from Henry's formula, then it is found that the energy (actually ζ^2) for the 2–2 type must be multiplied by a factor varying from 0.95 to 0.85, assuming that ζ for the 3–3 type is correct. This correction therefore appears to increase the discrepancy between the two cases.* However, Henry neglected the relaxation effect and also the other factors mentioned above need to be considered.

It is to be noticed that there is not much closer agreement among the values of (41) than among those of (40). This implies that for binary electrolytes (symmetrical type), the use of the complete Debye-Hückel equation is not vital in explaining the coagulating power of ions of different valencies. The approximate

[7] D. C. Henry, Proc. Roy. Soc. London **A133**, 106 (1931). See also, J. J. Hermans, Phil. Mag. **26**, 650 (1938) and S. Komagata, Res. Electrotech. Lab., Tokyo, No. 387 (1935).

* This may be overcome by replacing $\zeta=25$ mv for the 3–3 type in Table V by $\zeta\approx25\sqrt{0.9}\approx24$ mv roughly, so that Henry's correction term is not important. Since the mobility drops very rapidly with addition of trivalent coagulating ions, we may expect a larger error in detecting the critical ζ potential than with ions of lower valency.

Debye-Hückel theory leads to the ratio 9 : 4 for the coagulating concentrations of the 2–2 and 3–3 types, assuming the critical ζ potential to be the same. Experimentally, we obtain roughly 40 : 4 which seems quite different. However, our calculations show that a mere lowering of ζ from 30 to 25 mv is sufficient to account for the discrepancy. A similar behavior is exhibited by the energy calculated on the basis of the complete equation. (The latter situation is not surprising since for symmetrical electrolyte we have shown that the correction arising from considering the complete Debye-Hückel equation is not very large.†)

The preceding discussion leads us to a number of interesting conclusions. In I, it was stated that the form of the electrical energy corresponding to the approximate Debye-Hückel equation suggests that the value of ζ is not the only factor which determines precipitation. Thus, an examination of the results in Table V shows that for constant ζ, $F_2^0 - 2F_1$ decreases with τ (and also $F_2 - 2F_1$). However, since the energy is proportional to the square of the ζ potential, a relatively small change in ζ may be sufficient to counteract a much larger change in τ. In other words the energy is much more sensitive to a change in ζ. This property is indeed the origin of the close relation between the ζ potential and the stability of the sol. Further, when dealing with (41), which contains an additional term in ζ^4 the dependence on ζ becomes even stronger.

We may conclude from the above investigation that the agreement among the three types of electrolytes is about as good as one can hope to obtain. We have attempted to show that the coagulating powers of different ions depends on a number of factors which, indeed have not been clearly distinguished at all in most experiments.

An example of a theory which attributes the precipitating power of ions to one of the factors is that of Ostwald,[8] who maintains that coagulation should take place at the same activity coefficient of the precipitating ion, irrespective of the salt employed. Ostwald omits the monovalent ions which belong to the second type (easily adsorbed) introduced above and besides his results represent an average over an appreciable variation. Postponing a more detailed analysis of the apparent qualitative success of his principle until we have considered unsymmetrical electrolytes we shall be content with a few general remarks. Firstly, it has been shown that the ζ potential (intimately connected with the degree of ionic adsorption) is a determining factor in stability. Secondly, the radius of the particle must be considered as will be shown in another report to be published elsewhere.[9] It seems that his rule is mainly of an empirical character and that the reason for its qualitative validity in the cases which he considered is to be sought in a deeper analysis, such as has been attempted here.

In a further report, we shall extend our calculations to the unsymmetrical electrolytes, which are the more interesting and much better known. Here it will be found that the correction to the approximate Debye-Hückel equation is much larger, in agreement with the results of Müller.[5]

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Appendix

1. Calculation of radius of convergence X_0

An upper bound to the radius of convergence of the series (3) for ions was found by G.L.S. In order to obtain a lower bound than that estimated by them, we shall slightly modify their calcula-

† Only for large τ (large a) does the correction for the 3–3 type become important, and such values of τ have not been considered in Table V.

[8] See W. Ostwald, J. Phys. Chem. **42**, 981 (1938) for earlier references. Cf. H. B. Weiser, *Inorganic Colloid Chemistry* (Wiley and Sons, 1938), Vol. III, p. 190.

[9] S. Levine and G. P. Dube, Trans. Faraday Soc. (to be presented at the forthcoming discussion on "The Electric Double Layer").

tions. They showed that

$$|\zeta(u,\rho)| \leqslant \frac{e^{\tau-\rho}}{\rho}\frac{1}{2u}\left(e^{u-\tau}+\frac{\tau-1}{\tau+1}e^{\tau-u}\right), \tag{A.1}$$

where we have replaced their x by τ, $\rho=\kappa r$, and $\zeta(u,\rho)$ is the Green's function* associated with Eq. (1). When $r=a$, the equality sign holds. For a symmetrical binary type of electrolyte, we shall replace equation (45 G.L.S.) by

$$\mu=\frac{\beta}{1+\tau}+\frac{1}{2}\sum_{\nu=1}^{\infty}\frac{\mu^{2\nu+1}\tau^{2\nu}}{(2\nu+1)!}\int_{\tau}^{\infty}\left(e^{u-\tau}+\frac{\tau-1}{\tau+1}e^{\tau-u}\right)\frac{e^{(2\nu+1)(\tau-u)}}{u^{2\nu}}du \tag{A.2}$$

where, in our case $\beta=|\epsilon^2 Zz/kTDa|=3.605X$. The coefficients of μ^3 and μ^5 will be calculated exactly and those of the higher powers of μ will be replaced by upper bounds, adopting the procedure of G.L.S. In this way we obtain the following dominating series for (A.2)

$$\mu=\frac{3{,}605}{1+\tau}+\frac{\mu^3\tau^2}{6(1+\tau)}\{1-(1+\tau)e^{2\tau}E(2\tau)-2(\tau-1)e^{4\tau}E(4\tau)\}+\frac{\mu^5\tau^2}{720(1+\tau)}\{3-15\tau+26\tau^2$$
$$-32\tau^2(1+\tau)e^{4\tau}E(4\tau)-108\tau^2(\tau-1)e^{6\tau}E(6\tau)\}+\frac{\tau^2}{2(1+\tau)}\sum_{\nu=3}^{\infty}\frac{\mu^{2\nu+1}}{(2\nu+1)!(\nu-1+\nu\tau)}. \tag{A.3}$$

An approximate value for the radius of convergence $X=X_0$ of the series (4) (or equivalently of (3)) is obtained by solving the equation $dX/d\mu=0$ simultaneously with (A.3). The principle of this method has been explained by G.L.S.

2. Convergence of series (3i) (or (4i))

The integral equation, into which (1) was transformed by G.L.S. reads in our notation

$$\psi_0(\rho)=\frac{Q_0}{Da(1+\tau)}\frac{\tau e^{\tau-\rho}}{\rho}+\sum_{\nu=1}^{\infty}\frac{1}{(2\nu+1)!}\left(\frac{z\epsilon}{kT}\right)^{2\nu}\int_{\tau}^{\infty}\zeta(u,\rho)\psi_0{}^{2\nu+1}(u)u^2du. \tag{A.4}$$

If we write $\psi_0(\rho)=\zeta\chi_0(\rho)$ and then put $\rho=\tau$ $(r=a)$ (A.4) becomes

$$\zeta=\frac{Q_0}{Da(1+\tau)}-\frac{e^{\tau}}{1+\tau}\sum_{\nu=1}^{\infty}\frac{\zeta^{2\nu+1}}{(2\nu+1)!}\left(\frac{z\epsilon}{kT}\right)^{2\nu}\int_{\tau}^{\infty}e^{-u}\chi_0{}^{2\nu+1}(u)udu, \tag{A.5}$$

since $\chi_0(\tau)=1$ and $\zeta(u,\tau)=-e^{\tau-u}/(1+\tau)u$. This is actually the series expansion of Q_0 in powers of ζ and since it is necessarily unique, it must be identical with (4). To investigate the convergence of (A.5) we replace $\chi_0(u)$ by its upper bound, unity, and immediately derive the following dominating expression (series)

$$Q_0<Da(1+\tau)\frac{kT}{z\epsilon}\sinh\frac{z\epsilon\zeta}{kT}, \tag{A.6}$$

which converges for all finite ζ. A fair estimate of the three terms in ζ^7, ζ^9 and ζ^{11} in (A.5) follows on putting $\chi_0(u)=\tau e^{\tau-u}/u$, the form in the approximate Debye-Hückel theory. Then (A.5) becomes

$$\zeta\approx\frac{Q_0}{Da(1+\tau)}-\frac{e^{\tau}\zeta}{1+\tau}\sum_{\nu=1}^{\infty}\frac{(\tau e^{\tau}(z\epsilon/kT)\zeta)^{2\nu}}{(2\nu+1)!}\int_{\tau}^{\infty}\frac{e^{-2(\nu+1)u}}{u^{2\nu}}du. \tag{A.7}$$

* This should not be confused with the ζ potential, nor ρ introduced above with the charge density.

If we now replace the integral expression in (A.7) by the larger quantity $e^{-2(\nu+1)\tau}/\{2\nu-1+2(\nu+1)\tau\}\tau^{2\nu-1}$ (see G.L.S.) and then introduce X and Y in place of Q_0 and ζ, respectively, an estimate of the three terms in Y^7, Y^9 and Y^{11} in the series (4i) for X is readily found to be

$$0.277\tau^2\left\{\frac{\phi^7}{7!(5+8\tau)}+\frac{\phi^9}{9!(7+10\tau)}+\frac{\phi^{11}}{11!(9+12\tau)}\right\}, \quad \phi=1.20\times10^4 Y. \tag{A.8}$$

A comparison of (A.6) and (A.7) indicates the degree of accuracy of the approximate Debye-Hückel equation. If (A.6) were the solution of (1), then the error involved in using (1i) to derive the ζ potential would be represented by the ratio $\sinh(z\epsilon\zeta/kT)/(z\epsilon\zeta/kT)$. However, the first two terms in the series (A.7) in powers of ζ are readily seen to be identical with those in (4i) and each term in the series (A.6) is considerably greater than the corresponding one in (A.7). This means that the omission of all the terms higher than the first in (A.7), leading to the approximate solution, results in a much smaller error than does the same procedure in (A.6).

3. Expressions for quantities introduced in §4

The formulas given below have already been derived in II but are expressed here in a somewhat simpler form.

$$\delta_1(s,\tau)=\frac{e^{-\tau(s-2)}}{2s\tau}\left(\frac{\tau-1}{\tau+1}+e^{-2\tau}\right), \quad \delta_2(s,\tau)=\frac{e^{-\tau(s-2)}}{2s\tau}(1-e^{-2\tau}),$$

$$\delta_3(s,\tau)=\mu_2(s,\tau)-\mu_1(s,\tau),$$

$$\mu_1(s,\tau)=\frac{e^{-2\tau s}}{8s\tau}\{1-2\tau(s-2)+[2\tau(s+2)-1]e^{4\tau}\}-\frac{\tau(s^2-1)}{2s}e^{2\tau}\{E[2\tau(s-1)]-E[2\tau(s+1)]\},$$

$$\mu_2(s,\tau)=\frac{e^{-\tau(s-2)}}{s\tau}[1+\tau(s-2)-e^{-2\tau}].$$

4. Mutual internal energy of two particles (added in proof)

The original expression for U_2 is taken to be*

$$U_2=\tfrac{1}{2}\int_v\psi\rho dv+Q_0\bar{\Psi}(Q_0), \tag{A.9}$$

corresponding to (26). We now write the internal mutual energy as

$$U_2-2U_1=(Q_0^2/Da)f_1(s,\tau)+\{Q_0^4/(Da)^3\}(Z\epsilon/kT)^2g^*(s,\tau), \tag{A.10}$$

where

$$g^*(s,\tau)=2\{g_r(s,\tau)+g_a^*(s,\tau)\}, \tag{A.11}$$

corresponding to (33). According to the description at the end of §4 in the text, we obtain $g_a^*(s,\tau)$ from $g_a(s,\tau)$ as follows. The first term inside the square brackets, in the expression (35) for $g_a(s,\tau)$, is multiplied by $\frac{1}{2}$ and the second term by 5/7. The expression for U_2-2U_1 in powers of ζ follows from (37) on replacing $g(s,\tau)$ by $g^*(s,\tau)$ and denoting the resulting form for $G(s,\tau)$ by $G^*(s,\tau)$. On comparing the values of $g_a^*(2,\tau)$, $g^*(2,\tau)$ and $G^*(2,\tau)$ in Table VI, with those of $g_a(2,\tau)$ $g(2,\tau)$ and $G(2,\tau)$, respectively, in Table IV, it is seen that the latter quantities are not only considerably smaller in magnitude but may also differ in sign. In Tables II and III we have also shown the values of $13.0X_0^2g^*(2,\tau)$ and $1.44\times10^8Y^2G^*(2,\tau)$, respectively. An examination of these shows that, except at small τ (<1), the correction to the internal energy, arising from the consideration of the complete Eq. (1), is of the same order as the approximate energy calculated by means of (1i). This is in sharp contrast to the corresponding small correction to the energy function F_2-2F_1 computed in this paper. For large $s\gg1$, we find that

* We are neglecting the variation of D with T. Cf. N. Bjerrum, Zeits. f. physik. Chemie **119**, 145 (1926).

TABLE VI.

τ	$\ll 1$	0.1	0.3	0.5	0.8	1.0	2.0	3.0
$-10^3 g_a^*(2,\tau)$	$10^3\tau^2/6$	0.5113	0.9108	0.7528	0.4514	0.3154	0.06389	0.01875
$-10^3 g^*(2,\tau)$	$10^3\tau^2/2$	1.553	2.925	2.521	1.661	1.165	0.2770	0.09152
$-10^3 G^*(2,\tau)$	$10^3\tau^2/3$	1.216	2.970	3.298	3.166	2.676	1.499	0.9214
τ	4.0	5.0	6.0	7.0	8.0	9.0	10.0	$\gg 1$
$-10^3 g_a^*(2,\tau)$	0.007150	0.003239	0.001658	0.0009636	0.0005574	0.0003553	0.0002359	$\frac{11\times 10^3}{4608\tau^4}\left(1+\frac{29}{22\tau}\right)$
$-10^3 g^*(2,\tau)$	0.03808	0.01849	0.01001	0.005942	0.003666	0.002408	0.001644	$\frac{55\times 10^3}{2304\tau^4}\left(1-\frac{421}{110\tau}\right)$
$-10^3 G^*(2,\tau)$	0.6197	0.4448	0.3342	0.2615	0.2080	0.1704	0.1420	$\frac{43\times 10^3}{2304\tau^2}\left(1-\frac{249}{86\tau}\right)$

$g^*(s,\tau)\approx 2g_a^*(s,\tau)\approx g_a(s,\tau)\approx g(s,\tau)$ and $G^*(s,\tau)\approx G(s,\tau)$ so that at large separations the two definitions of the mutual energy lead to the same results. This suggests that the difference between the two is a maximum at or near contact position of the two particles and then diminishes as the particles move apart.

The quantity that should be considered when dealing with the interaction of colloidal particles is, of course, the "free energy" of charging all the particles and ions, for fixed positions of the particles. The quotation marks are to remind us that strictly one should only use the term free energy for a measurable quantity but the formal expression for the energy to be evaluated is that of a free energy so that we shall adopt this terminology. In II, a tentative theory was developed showing that for sufficiently dilute sols the problem reduces to calculating F_2-2F_1, the mutual energy of two particles, the assumption being made that κ is constant during the charging process. The fact that such different results are obtained by the two methods described above shows that one must be careful in choosing the appropriate expression for the energy. In particular, it would be desirable to investigate the error involved in assuming κ constant. We hope to return to the latter problem later.

Note on the Solvent Effect in Dipole Moment Measurements

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THE experimental work of Müller[1] and others has definitely established the existence of a solvent effect in dielectric polarization measurements. The effect has been shown to influence only the orientation polarization. Thus, for example, the molar orientation polarization of nitrobenzene measured in benzene is 330 cc whereas it is 380 cc if measured in the gas state.

Considerable work has been done on this problem[2] both theoretically and empirically. In general, however, the actual application of solvent effect corrections has been largely of an empirical nature. A new and promising theoretical approach is offered by the use of the Onsager[3] reaction field. The reaction field, R, is the electric field which acts on a dipole as a result of displacements induced on the surrounding medium by the dipole. Onsager has shown that R is given, for a rigid dipole of strength μ at the center of a cavity of volume $1/n$, by the expression

$$R=\frac{4\pi n}{3}\left(\frac{2\epsilon-2}{2\epsilon+1}\right)\mu. \tag{1}$$

Here n is the number of molecules per cc and ϵ is the dielectric constant of the medium. The application of R to explain solvent influences is made, in this paper, by using an equation given by Böttcher[4] which equation shows that the van Arkel and Snoek[5] equation for the molar orientation polarization is really the original Debye relation modified by a term containing the Onsager reaction field. Böttcher's equation is

$$P_0=\frac{4\pi N}{3}\left(\frac{\mu^2}{3kT+\mu R}\right), \tag{2}$$

where N is Avogadro's number, R the reaction field, and the other symbols have their usua meaning. It is evident from (2) that the dipole of strength μ is bound to its reaction field with an energy μR. Simply on the basis of this binding one would expect a significant reduction in the value of P_0. It must be remembered, however, that if R acts on a molecule of polarizability α it will induce a moment in this polarizability, which moment would tend to increase P_0. This last effect shows that the picture of the rigid dipole to which Eq. (1) is applicable, is an idealized one, and in view of this and other possible imperfections of theory, it is not surprising that on calculation of μR and P_0, a larger reduction in P_0 than that observed is found. The magnitude of the observed reduction caused by solvent influences is obtained by comparing the P_0 value from the gas measurement (where $\mu R\rightarrow 0$) with the P_0^∞ from a solution measurement. P_0^∞ is the molar orientation polarization extrapolated to infinite dilution in the nonpolar solvent. In all cases considered here it is assumed that P_0^∞ is given by

$$P_t^\infty - M_D = P_0^\infty, \tag{3}$$

where P_t^∞ is the total molar polarization at infinite dilution, and M_D is the molar refraction for the Na_D line. No account is taken of the atomic polarization as this would introduce an uncertain and unnecessary refinement.

Since Eq. (2), as written, is inadequate, the assumption is made that P_0^∞ is given by

$$P_0^\infty=\frac{4\pi N}{3}\left(\frac{\mu^2}{3kT+C'\mu R}\right), \tag{4}$$

where C' is a constant independent of the nonpolar solvent and characteristic for the particular dipole molecule. C' is evaluated by Eq. (5)

$$P_{0(g)}/P^\infty{}_{0(s)}=1+C'\mu R/3kT, \tag{5}$$

where $P_{0(g)}$ is the molar orientation polarization in the gas state, and $P^\infty{}_{0(s)}$ is the same quantity in benzene solution in which the reaction field is R. The same value of C' is then used in Eq. (4)

[1] F. H. Müller, Physik. Zeits. **34**, 701 (1933).
[2] F. C. Frank, Proc. Roy. Soc. (London) **A152**, 171 (1935); K. Higasi, Bull. Inst. Phys. Chem. Res. (Tokyo) **14**, 146 (1935); J. Weigle, Helv. Phys. Acta **6**, 68 (1933); R. J. W. Le Fevre, J. Chem. Soc. 773 (1935).
[3] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).
[4] C. J. F. Böttcher, Physica **5**, 635 (1938).
[5] A. E. van Arkel and J. L. Snoek, Physik. Zeits. **33**, 662 (1932); Trans. Faraday Soc. **30**, 707 (1934).

TABLE I. *Nonpolar solvent influences (20°C).*

SOLVENT	GAS	HEXANE	DECALIN	CCl_4	C_6H_6	C_2Cl_4	CS_2
ϵ	1.00	1.91	2.16	2.24	2.28	2.29	2.64
V (cc)	—	126	157	97	88	103	60
Solute				P_0^∞ (cc)			
C_6H_5Cl Calc.	—	54	54	51	(50)	51	45
C_6H_5Cl Obs.	61	55	52	50	50	48	44
$C_6H_4Cl_2$ Calc.	—	114	114	110	(109)	111	102
$C_6H_4Cl_2$ Obs.	121	113	109	—	109	—	94
$n-C_3H_7Cl$ Calc.	—	82	83	79	(78)	79	72
$n-C_3H_7Cl$ Obs.	88	83	82	80	78	78	69
CH_2Cl_2 Calc.	—	53	53	52	(52)	52	50
CH_2Cl_2 Obs.	55	56	53	54	52	—	46
$(CH_3)_2CO$ Calc.	—	163	164	160	(160)	161	154
$(CH_3)_2CO$ Obs.	170	167	159	176	160	—	154
$C_6H_5NO_2$ Calc.	—	348	351	336	(330)	336	303
$C_6H_5NO_2$ Obs.	380	346	350	331	330	—	295

for calculating P_0^∞ for the dipole in the other nonpolar solvents. The calculation of μR has been made by Eq. (6)

$$\mu R=\frac{25.2}{V}\left(\frac{2\epsilon-2}{2\epsilon+1}\right)\frac{\mu^2}{10^{-23}}, \qquad (6)$$

where V is the molar volume and ϵ is the dielectric constant of the nonpolar solvent, and μ is the dipole moment of the dipolar molecule. The use of ϵ, and V for the pure solvent is valid in the limit of infinite dilution.

In Table I are shown the values of P_0^∞ observed by Müller[1] in various solvents compared with the values calculated by the above method. Using measurements in benzene as solvent leads to values of C' of 0.63, 0.18, 0.31, 0.21, 0.074, 0.078 for chlorobenzene, *o*-dichlorobenzene, *n*-propyl chloride, methylene chloride, acetone, and nitrobenzene, respectively. The values of P_0 in the gas state are calculated using the following values (in debyes) for the moments: chlorobenzene 1.70, *o*-dichlorobenzene, 2.40, *n*-propylchloride 2.05, methylene chloride 1.62, acetone 2.85, and nitrobenzene 4.25.

The agreement between observed and calculated values is quite satisfactory especially for the purpose of dipole moment calculations since $\mu \propto (P_0)^{\frac{1}{2}}$. Müller[6] has measured chlorobenzene in nineteen other solvents in addition to those listed in Table I. On applying the method to these cases the general trend is correct except in four cases, three of which involve polar solvents. The polar solvents should properly be excluded as the constant C' was established for solvents of the nonpolar type.

It is well known that some cases of a positive solvent effect exist, and they, in general, are not explicable by the present method unless C' assumes a negative value. It should be pointed out, however, that compound formation, or high energy associations should be definitely excluded before the positive effects are taken too seriously. The most obvious exception in Table I is acetone in carbon tetrachloride, which is explained by Müller as a case of an acetone-carbon tetrachloride aggregate. The field of complex formation in mixtures has been investigated by Earp and Glasstone[7] and good evidence of intermolecular formations has been obtained in many cases.

[6] F. H. Müller, Physik. Zeits. **38**, 286 (1937).
[7] D. P. Earp and S. Glasstone, J. Chem. Soc. 1709 (1935).

A Note on the Construction and Operation of a Thermal Diffusion Column for the Separation of Isotopes

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SINCE the demonstration by Clusius and Dickel[1] that the Chapman effect coupled with a thermal syphon action could be used to separate isotopes, a number of investigators have started both theoretical and experimental studies on such columns.[2]

We have constructed a 40-foot column in which the cold surface is a two-inch standard galvanized pipe concentric with a one-inch pipe for the hot surface. This leaves an annular space of 9 mm with a mean circumference of 13.8 cm for the methane. A water jacket made of four-inch standard pipe surrounds the two-inch pipe for cooling purposes. An oxygen tank was welded on top to give a volume of 30 liters above the annular space. A one-liter glass flask fastened with a sealing wax joint to the two-inch pipe gives a total volume of 40 liters. The sampling and evacuating system along with the manometer and Pirani gage are attached to the liter flask. The one-inch pipe is closed at the lower end and is suspended from the top of the oxygen cylinder such that there is a clearance of two inches at the bottom to allow for expansion. Four sets of three steel pins each maintain the spacing in the annular space uniform. These are made from $\frac{1}{8}$-inch steel rod tapered to obtain a small point of contact with the cold surface.

The first heating element used was constructed of two loops of No. 16 nichrome wire in parallel insulated from the inside of the one-inch pipe by means of three-inch porcelain insulators ($\frac{1}{4}$ in. hole, $\frac{1}{16}$ in. wall thickness). Connection to a 220-volt line through suitable rheostats was made with heavy copper wire just below the cylinder. A second heating element was made with the same insulators using No. 14 nichrome wire covered with an asbestos sheath. These heating elements were unsatisfactory because there was not adequate provision for thermal expansion and moisture from the asbestos sheathing distilled to the top part of the column. The third heating element was constructed from one loop of No. 10 nichrome wire enclosed in double bore oval insulators (3 in.$\times\frac{1}{2}$ in.$\times\frac{1}{4}$ in.). These in turn were placed in a system of cylindrical insulators ($5\frac{1}{2}$ in.$\times\frac{9}{16}$ in. bore$\times\frac{3}{32}$ in. wall thickness). The whole was enclosed in a woven copper sheath for easy removal. Two thermocouples were imbedded in the outside of the one-inch pipe three feet from the top and bottom, respectively, and brought out through sealing wax joints.

Several experiments were performed to study the operation and behavior of the column. The abundance ratio of $C^{13}H_4$ was changed by a factor of about 2 (see Table I).

In experiments I and II using the first and second heating elements, respectively, the temperature at the two ends of the one-inch pipe were nearly the same. In Experiment III with the third heating element, however, the difference between the two ends was about 100°C. The reason for this difference in behavior of the two types of heating elements may lie in their construction in the sense that different convection currents exist within the one-inch heating tube. We have studied this point with the second heating element by filling the spaces between the insulators and the pipe with sand. However, the temperature difference between the top and bottom persisted, while the average temperature dropped from 291°C to 226°C with 0.1 mm pressure in the annular space and to 188° with 1 mm

TABLE I.

Experiment	Kilowatts	mm Hg CH_4	Cold Temp.	Ave. Hot Temp. °C	Time	Percent $C^{13}H_4$
I	3.68	180	20	236	max. conc.	2.2
II	8.40	170	20	330	$2\frac{1}{2}$ days	2.4
III	5.27	700	20	264	2 days	2.0

[1] Clusius and Dickel, Naturwiss. **26**, 546 (1938); **27**, 148 (1939).

[2] Brewer and Bramley, Phys. Rev. **55**, 590 (1939); Furry, Jones and Onsager, Phys. Rev. **55**, 1083 (1939); Gillespie, J. Chem. Phys. **7**, 530 (1939).

pressure using the same wattage. The average temperature and the temperature difference increased as the pressure in the annular space was progressively decreased. This seemed to indicate that the remaining gas inside the one-inch heating tube still carried heat to the top. We therefore evacuated the heating unit with the result that the temperature at the top and bottom reach the same value with a low pressure in the annular space. These points are being studied further because they may be of importance in the extent of separation.

It is important to use pure methane in the experiments since the heavy impurities will concentrate at the bottom and may interfere with the separation. This is shown by the relative heights of the peaks for the following masses on a mass spectrometer: Original methane for Exp. I and II: mass 16 (100); 17 (1.9); 28 (21); 30 (2.2); 32 (1.) and 44 (1.8). Final gas: mass 16 (100); 17 (3.2); 28 (128); 30 (9.6); 32 (6.5) and 44 (6.7). This sample of methane was prepared by distillation at liquid-air temperature by using a standard Podbielniak low temperature fractionating column arranged for analytical purposes and fitted with rubber connections. Evidently masses 28, 30, 32 and 44 were not removed efficiently. Owing to differences in ionizing efficiencies, the mass spectrometer does not give the correct values for the relative abundance of molecules in a gas mixture. This was further shown by the ratio of mass 16 to 28 in a gas bought as 96 percent methane, this ratio being 100 to 80 for the height of the peaks. In order to determine the usefulness of the mass spectrographic method for analyzing gases, a known mixture of nitrogen and methane containing 80 percent of the latter was analyzed in the same apparatus. The relative heights of the peaks were found to be 16 (100) and 28 (160). That is, the nitrogen peak is of the order of eight times higher than one would predict for equal ionizing efficiencies. However, the mass spectrometer does afford a satisfactory method of comparison of one sample with another. From the above figures it is also seen that mass 28 as well as the other impurities increases over fivefold which may markedly affect the separation attained in a given column.

In order to obtain very pure methane, we constructed an all glass distilling system and prepared a gas sample for Experiment III showing the following relative peaks: mass 16 (100); 17 (1.29); 28 (0.6); 30 (0.02); 32 (0.002); 44 (0.04). Final values: mass 16 (100); 17 (2.0); 28 (12.7); 30 (0.1); 32 (0.002); 44 (0.1). It is seen that this was a much purer sample of gas but the impurities concentrate several-fold in the lower sections of the column. By drawing these gases off, a further purification of the methane can be achieved.

When the results obtained so far are not as encouraging as the theory[2] would predict for this type of column, it is hoped that elimination of some of the difficulties described may give the predicted results. The optimum conditions of temperature, pressure, heavy carbon supply, surface, and space separation are yet to be determined. It is also not known whether a column with concentric tubes is as effective as a hot wire, although its capacity is greater.

We are greatly indebted to Professor A. O. Nier of the Physics Department for carrying out the spectrographic analyses.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Infra-Red Absorption Spectrum of Normal Pentane

The absorption spectrum of normal pentane in the region from 1.0μ to 16.μ has been examined using a Wadsworth-Littrow type of prism spectrometer. A rocksalt prism was used to produce the dispersion and a Moll thermal relay to amplify the deflections. All of the absorption regions reported by Kettering and Sleator[1] have been confirmed and new peaks located. In general the envelope of the bands showed somewhat more detail than that given by Sleator and Kettering.

Certain regions were further examined under the high dispersion produced by a prism-grating spectrometer. This further improved the detail of the envelope, indicating a double structure in the bands at 6.8μ and 7.2μ and definitely showing a doublet in the narrow band at 7.9μ. The separation of the doublet in each case is approximately 10^{-1} cm.

In the region from 8.0μ to 8.5μ a series of ill-defined peaks, separated by about 2.0 cm^{-1} seemed to be present. Although others working with this instrument in the same region have been able to separate lines considerably closer together than these, yet efforts to obtain further detail here proved fruitless.

The model of the pentane molecule is usually taken to be of a W form, with a carbon atom at each point of the W. The C−C−C bond angles are tetrahedral. Three hydrogen atoms are attached to the first and last carbon atoms forming methyl groups, and two hydrogen atoms are attached to each of the other three carbon atoms. Assuming the data suggested by Wierl[2] for such a model, one may arrive at the approximate values of 2.2×10^{-39} g cm^2 for the smallest moment of inertia and 4.2×10^{-38} for the largest.

Dennison and Gerhard[3] have developed a theory for the envelopes of the absorption bands of polyatomic molecules which leads one to expect parallel-type bands in which the Q branch is relatively weak. If one takes the value of 10. cm^{-1} as the distance between the most intense portions of the P and R branches, one may estimate, by the aid of this theory, the value of 4.5×10^{-38} for the larger moment of inertia. This is in excellent agreement with the value suggested above from the model.

If one further identifies the poorly defined spacings in the 8.4μ region with the separation of the Q branches of a perpendicular type band, a value of 2.6×10^{-39} may be arrived at as the value of the smallest moment of inertia. This also is in good agreement with the value from the model.

While the above results must certainly be taken with some reservations, they seem of sufficient importance to place on record.

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July 19, 1939.

[1] Kettering and Sleator, "The Infrared Absorption Spectra of Certain Organic Compounds," Physics **4**, 2 (1933).
[2] R. Wierl, "Molecular Structure of Butane and Pentane," Arm. Phisik **8**, 521–64 (1931).
[3] Gerhard and Dennison, "The Envelope of the Infra-Red Absorption Bands," Phys. Rev. **43**, 197–204 (1933).

On Some Properties of White Sapphire

Plane transparent windows of white sapphire can be obtained as large as $2''\times\frac{1}{2}''\times\frac{1}{16}''$ at no great cost.[1] Each window is cut from a single synthetic crystal of corundum (pure aluminum oxide). They show excellent transmission throughout the visible region of the spectrum and in the ultraviolet to about 1435A.[2]

Corundum is uniaxial and can presumably be cut in the proper orientations for analyzers and polarizers of radiation and the same technique which has served so well with quartz can be extended for regions further in the ultraviolet. The only published data which were found on the birefringence of sapphire (in the visible region of the spectrum) showed it to be of about the same magnitude as that of quartz. Fluorite although more transparent than white sapphire is optically isotropic.

The high chemical stability of crystalline aluminum oxide suggested that it might withstand corrosive liquids and gases for which no suitable windows are known. In experiments being carried out here on the Raman effect of liquid hydrogen fluoride, white sapphire windows have remained unimpaired despite fifteen hours' contact with liquid and gas.

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August 1, 1939.

[1] We are indebted to the Heller Hope Company in New York for their cooperation in supplying us with these sapphire placques.
[2] A window one millimeter thick was placed for forty minutes across a beam of radiation from a hydrogen discharge operating at a out 12,000 volts direct current. A few lines at 1434A were distinctly transmitted in the vacuum spectrograph. At 1440A the lines were rather intense. Eastman Hyperprocess Plates were employed together with Eastman Ultraviolet Sensitizer. The grating ruled with 5910 lines per centimeter had a focal length of two meters and was adjusted at a grazing incidence of 78 degrees.

The Separation of Gases by Diffusion

Classical methods of atmolysis depend either upon reducing the pressure of a gas mixture to be separated to such a point that the mean free path of the molecules assumes macroscopic dimensions, as in a diffusion pump, or by use of solid septa having passages of the order of magnitude of intermolecular dimensions at ordinary pressures, so that gas molecules may pass through them relatively free from collision with other gaseous molecules. Either method results in capacities that are infinitesimal, based on the volume of gas treated as measured under normal conditions.

For the past several years, work of a technical nature has been going on at the Pacific Experiment Station of the Bureau of Mines, U. S. Department of the Interior, to separate gases of different molecular weights by diffusion at normal pressures, and this work has been highly successful. Separations comparable to the perfect functioning of Graham's law, no matter what the initial composition of gas treated, have been shown possible at rates that are enormous when compared to the classical methods, or to the recently much investigated methods of thermal diffusion.

The method used is extremely simple and is based upon the realization that if the constituents of a binary mixed gas diffuse into a third gas, the relative rate of diffusion of the constituents will in general be close to the Graham's law ratio. We have made the third gas steam, or any condensible vapor, provided a short diffusion path, and attached a regulating valve and two condensers to the atmolyzer unit.

The device is in essence a diffusion boundary, whose only purpose is a hydrodynamical one of separating the flow of two streams of fluid contiguous to one another. The apertures connecting the streams may be of any convenient size, a suitable screen being ordinary perforated sheet brass, 26 gage, 625 perforation per sq. in., each perforation nominally $\frac{1}{64}$ in. diameter. Steam is made to flow uniformly along one side of such a boundary, which may be conveniently cylindrical, and the gas to be separated is caused to flow countercurrently along the opposite side. A throttle valve in the steam line adjusts the static pressures on opposite sides of the boundary to a close approximation of balance, and under these conditions the stream of gas is divided into two fractions, in proportions that are changed at will by adjustment of the valve, whereupon the gas issuing into the steam duct will be found after condensation of vapor to be greatly enriched. The lesser the fraction diffusing into the vapor stream, the lower the extraction and the greater the ratio of concentration. Using a flow of vapor sufficiently great, back diffusion is prevented, and a maximum constant concentration gradient maintained.

The imposition of a mass motion upon the diffusive flow, per or contra, enables all degrees of ratio of concentration to be obtained, exceeding those given by Graham's law for a condition in static pressure balance.

Some idea of the effectiveness of this method may be gained from the following approximate performance under conditions technically interesting for the separation of hydrogen from nitrogen or carbon monoxide: (1) Original gas 30 percent hydrogen, in one pass produces 55–65 percent product with an extraction of 75–85 percent. (2) Second pass produces 75–85 percent product, with similar yield. (3) Third step produces gas better than 98 percent H_2. (4) Area of diffusion boundary 60–75 sq. cm. (5) Capacity 0.5 to 1.0 liter per minute of product. (6) Steam consumption approximately 2–3 grams per liter of product per stage. (7) Operating temperature 135–150°C, pressure near atmospheric.

The writer has been interested primarily in the many possible technical applications of such methods. He commends it to the attention of those interested in isotopes, a subject he is unable to develop himself. The methods and apparatus are the subject of a patent application, assigned to the U. S. Secretary of the Interior for administration in public interest, and the process may presumably be licensed without cost. A bulletin describing the results of more than 3000 tests of various types of diffusion boundaries is in course of preparation and will discuss in detail the theory and practise of technical atmolysis by this method.

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July 17, 1939.

Interpretation of the Visible Absorption of Bromine

Recent work on the visible bromine continuum in solution[1, 2] together with data from Brown[3] and Darbyshire,[4] can be used to decide between Mulliken's alternative interpretations[5] of the A and B components,[6] namely—

$$A \quad \begin{cases} {}^1\Pi_u \leftarrow {}^1\Sigma_g^+ \\ {}^3\Pi_{0^+u} \leftarrow {}^1\Sigma_g^+ \end{cases} \qquad (1)$$

$$B \quad {}^3\Pi_{1u} \leftarrow {}^1\Sigma_g^+$$

Coupling—$\Omega - s$.

and

$$A \quad {}^1\Pi_u \leftarrow {}^1\Sigma_g^+ \qquad (2)$$

$$B \quad \begin{cases} {}^3\Pi_{0^+u} \leftarrow {}^1\Sigma_g^+ \\ {}^3\Pi_{1u} \leftarrow {}^1\Sigma_g^+ \end{cases}$$

Coupling—$\Lambda - \Sigma$.

Although (2) has been established for chlorine,[7] Mulliken suggests that (1) is more probable for the comparatively heavy bromine molecule.

Since the perturbations due to neighboring solvent molecules will cause the further breakdown of selection rules that are already violated in the gas, (2) would mean that solvents should enhance the B component more than A, since B would contain the "forbidden" intersystem transitions, Σ being a good quantum number. This is opposed to the experimental data, which show B to be affected but little, while A is increased some 30 percent. With $\Omega - s$ coupling (1), however, Σ is no longer a good quantum number and intersystem transitions should not be enhanced by perturbations. In this case, the only violation of a selection rule is that of $\Delta\Omega_c = \Delta\Lambda_c$ by ${}^3\Pi_{0^+u} \leftarrow {}^1\Sigma_g^+$, occurring in the A continuum which experiment shows to be enhanced.

Bayliss[8] and Darbyshire[4] have produced Franck-Condon evidence in favor of (2), including the correspondence of the $U'(r)$ curve calculated from the B continuum with the Morse curve calculated from the band data on ${}^3\Pi_{0^+u}$. Since (2) requires the $U'(r)$ curve for B to be an average of two,

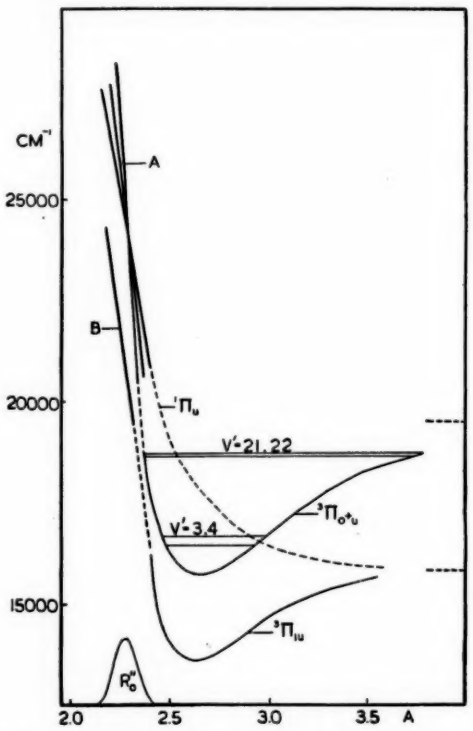

FIG. 1. Potential energy—nuclear separation curves for bromine. Curves marked *A* and *B* are calculated from the continuum.

and since Morse curves are generally incorrect for high v', this correspondence is probably fortuitous. On interpretation (1), the calculated $U'(r)$ curve for *A* must be an average curve, and theoretical work on the effect of solvents makes it appear that it consists of two components crossing at approximately 24,000 cm^{-1}. Unpublished theoretical considerations have shown that, in associated solvents such as water, the $U''(r)$ curve for $^1\Sigma_g^+$ is displaced to slightly smaller r'' values. In the case of water, it is required to displace the v_0'' eigenfunction some 0.02A to smaller r'' values. In such a case, the two $U'(r)$ curves crossing at 24,000 cm^{-1} would cause the two superimposed maxima in component *A* to separate, leading to a broadening of the *A* continuum with little change in ϵ_{max}, as is observed. This is borne out by the fact that the integrated intensity is approximately the same as in other solvents.

The $U(r)$ curves for the various states have been constructed in a semi-quantitative way and are illustrated in the accompanying Fig. 1. The $U'(r)$ curve for *B* extrapolates reasonably to the Morse curve for $^3\Pi_{1u}$, obtained by Darbyshire on what he considers to be the most probable numeration. Such a system of $U(r)$ curves requires $^1\Pi_u$ to cross $^3\Pi_{0^+u}$ at about 16,500 cm^{-1} and $^3\Pi_{1u}$ to approach $^3\Pi_{0^+u}$ very closely at about 18,700 cm^{-1}, at both of which points perturbations in the vibrational levels of the $^3\Pi_{0^+u}$ state should occur. It is significant that Darbyshire[4] observed anomalies which led him to conclude that the $v'=3$ and 4 levels of $^3\Pi_{0^+u}$ were perturbed and that these vibrational levels lie close to 16,500 cm^{-1}; and also that Brown[3] observed a change in the law of force for vibrations in the region of the levels $v'=21$ and 22 for the same $^3\Pi_{0^+u}$ state, that is, at about 18,700 cm^{-1}.

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[1] Aickin, Bayliss and Rees, Proc. Roy. Soc. London **A169**, 234 (1938).
[2] Child and Walker, Trans. Faraday Soc. **34**, 1506 (1938).
[3] Brown, Phys. Rev. **39**, 777 (1932).
[4] Darbyshire, Proc. Roy. Soc. London **A159**, 93 (1937).
[5] Mulliken, J. Chem. Phys. **4**, 620 (1936).
[6] Acton, Aickin and Bayliss, J. Chem. Phys. **4**, 474 (1936).
[7] Aickin and Bayliss, Trans. Faraday Soc. **33**, 1333 (1937).
[8] Bayliss, Proc. Roy. Soc. London **A158**, 551 (1937).

Fluorescence of Glyoxal Vapor

Matheson and Zabor* have described in this journal some measurements on the fluorescence of certain aldehydes and ketones, the similarity of which to each other suggests that a common product of photolysis is responsible for the fluorescence. Although both experimentally and otherwise I am in agreement with their conclusions, it may be of interest to report measurements on the fluorescence of another dialdehyde, glyoxal vapor, which indicate a different mechanism for the fluorescence in this case. This result might have been expected since the glyoxal molecule contains no methyl groups. Glyoxal vapor shows two systems of absorption in the near ultraviolet, namely *ca.* 4600–3400A and *ca.* 3200–2300A, respectively. The bands of the former region have been studied under low dispersion and in the third order of a 21-foot grating, and reveal a system of discrete bands with remarkably fine structure; the other absorption region to higher frequencies appears to be composed of diffuse (predissociated) bands. With a view to obtaining help in the vibrational and rotational analysis of the discrete band system, the fluorescence of the vapor has been photographed, by using as exciting frequencies the lines emitted by a mercury vapor lamp 3600–4400A, and a glass prism spectrograph of high aperture and resolving power, having a dispersion of about 40A per mm at 4400A. A well-marked system of sharp bands is observed in fluorescence between 4200–5200A, the strongest bands being in the blue-green, and particularly that at *ca.* 4780A. This band system is unlike the fluorescence emission spectrum of any other simple aldehyde or ketone, and in particular may be contrasted in both spectral region and structure with that shown by formaldehyde when the latter molecule is irradiated with ultraviolet frequencies. It is hoped shortly to suggest a detailed vibrational analysis of the fluorescence spectrum together with a partial analysis of some of the absorption bands. Although the latter appear to be very complicated, the nature of the fine structure of certain bands suggests that the moments of inertia of the molecule are such that the molecule must exist in the *trans*-form, which has also been considered in the case of the electronically closely related molecule butadiene $CH_2 : CH.CH : CH_2$.

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* Matheson and Zabor, J. Chem. Phys. **7**, 536 (1939).

Anharmonicity of CH Vibrations and Product Rule

Applications of the product rule, derived by Teller[1] and the author,[2] have been impaired to some extent by the anharmonicity of hydrogen vibrations which causes discrepancies a little larger than common experimental errors. Anharmonicity is connected by Morse's formula[3] with dissociation energy and the latter is known to be approximately the same for all CH bonds. It may be expected, therefore, that deviations due to anharmonic character of CH vibrations are eliminated with sufficient accuracy if the same correction is applied to vibrations of similar kind.

The anharmonicity factor x may be taken, according to Ellis,[4] as 2.2 percent for an aliphatic and 1.9 percent for an aromatic hydrogen valency vibration. The correction to be applied to the quotient of corresponding valency vibrations of hydrogen and deuterium[5] amounts to $x(2-\sqrt{2})$ $=1.3$ percent and 1.1 percent, respectively.

The applications of the product rule to compounds with CD bonds are listed in Table I. The column headed "V" contains the number of D valency vibrations involved, column "B" the number of bending or deformation vibrations. The differences between the calculated and observed product values and the suggested correction for anharmonicity are given in percents.

The average difference in 34 cases involving valency vibrations amounts to 1.62 percent and agrees satisfactorily with the average correction 1.42 percent. The individual discrepancies, considerable though unsystematic, are explained by experimental error. The discrepancies are remarkably less in the cases of totally symmetrical frequencies which, as a rule, can be determined more precisely.

TABLE I. *Product values and anharmonicity correction.*

Substance	Symmetry	V	B	Prod. Calc.	Prod. Obs.	Diff. %	Corr. %	Ref.
CH_3D	A_1	1		1.370	1.354	1.2	1.3	6
	E		1	1.179	1.170	0.8	—	
CH_2D_2	A_1	1	1	1.881	1.823	3.1	1.3	
	A_2		1	1.155	1.181	−2.3	—	
	B_1	1	1	1.437	1.416	1.5	1.3	
	B_2		1	1.204	1.197	0.6	—	
CHD_3	A_1	1	1	1.833	1.810	1.1	1.3	
	E	1	2	2.046	2.083	−1.8	1.3	
CD_4	A	1		1.414	1.398	1.1	1.3	
	E		1	1.414	1.444	−2.1	—	
	F	1	1	1.788	1.768	1.1	1.3	
C_2D_2	A_1	1		1.414	1.398	1.1	1.3	7
C_2D_4	A_{1g}	1	1	1.998	1.954	2.2	1.3	8
	A_{2g}	1	1	1.666	1.624	2.5	1.3	
	A_{1u}	1	1	1.868	1.827	2.2	1.3	
C_2D_6	A_1	1	1	1.998	1.91	4.5	1.3	9
	A_2	1	1	1.82	1.79	1.7	1.3	
	E	1	2	2.58	2.44	5.4	1.3	
$CHCl_3$	A_1	1		1.407	1.378	2.1	1.3	10
	E		1	1.398	1.382	1.1	—	
$CHBr_3$	A_1	1		1.411	1.400	0.8	1.3	11
	E		1	1.406	1.409	−0.2	—	
CH_2Br_2	A_1	1	1	1.986	1.95	2.0	1.3	12
cis-$C_2D_2Cl_2$	A_1	1	1	1.978	1.915	3.2	1.3	13
trans-$C_2D_2Cl_2$	A_1	1	1	1.985	1.883	5.1	1.3	
$C_2D_4Br_2$	A_1	1	2	2.82	2.76	2.1	1.3	14
CD_2O	A_1	1	1	1.936	1.900	1.9	1.3	15
	B_1	1	1	1.662	1.715	−3.2	1.3	
	B_2		1	1.168	1.241	−6.2	—	
o-$C_6H_4D_2$	B_1	1	1	1.909	1.881	1.5	1.1	16
m-$C_6H_4D_2$	A_1	1	1	1.975	1.972	0.2	1.1	
p-$C_6H_4D_2$	A_{1g}	1		1.414	1.397	1.2	1.1	
vic-$C_6H_3D_3$	A_1	2	1	2.776	2.790	−0.5	2.2	
sym-$C_6H_3D_3$	E'	1	1	1.959	1.97	−0.6	1.1	
o-$C_6H_2D_4$	B_1	2	2	3.655	3.572	2.3	2.2	
m-$C_6H_2D_4$	A_1	3	1	3.901	3.901	0.0	3.3	
p-$C_6H_2D_4$	A_{1g}		1	1.414	1.442	−2.0	—	17
	B_{1g}		1	1.286	1.283	0.2	—	17
	B_{2g}	1		1.370	1.350	1.5	1.1	17
C_6HD_5	A_1	3	2	5.484	5.291	3.5	3.3	
C_6D_6	A_{1g}	1		1.414	1.402	0.8	1.1	
	E_g^+	1	1	1.998	1.941	2.9	1.1	
	E_g^-		1	1.288	1.280	0.6	—	
	E_u^-	1	1	1.925	1.931	−0.3	1.1	

It may be noted that the ten cases involving only a bending frequency seem to indicate a small negative anharmonicity factor. The third-order term in a power series of the potential energy must necessarily result in a positive value of this factor (cf. reference 5). It may be concluded, therefore, that the third-power term is zero or, at least, small. This is precisely what is to be expected in bending vibrations. The two halves of a bending vibration are in some molecules exactly, in others at least approximately alike. So we may expect, indeed, that the odd terms of the potential energy series vanish. The experimental material available will hardly justify a quantitative conclusion.

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[1] Cf. C. K. Ingold *et al.*, J. Chem. Soc. London 971 (1936).
[2] O. Redlich, Zeits. f. physik. Chemie **B28**, 371 (1935).
[3] P. M. Morse, Phys. Rev. **34**, 57 (1929).
[4] J. W. Ellis, Phys. Rev. **33**, 27 (1929). Ta-You Wu and A. T. Kiang, J. Chem. Phys. **7**, 178 (1939), found 2.1 percent and 1.5 percent for the hydrogen valency vibrations of acetylene.
[5] Cf. C. Manneback, Ann. Soc. Scient. Bruxelles **B55**, 237 (1935).
[6] G. E. MacWood and H. C. Urey, J. Chem. Phys. **4**, 402 (1936). W. S. Benedict, K. Morikawa, R. B. Barnes and H. S. Taylor, J. Chem. Phys. **5**, 1 (1937). The average of Raman and infra-red values has been used where both have been determined. The product formulae are, of course, identical in this case with the corresponding equations derived by J. E. Rosenthal, Phys. Rev. **45**, 538 (1934).
[7] G. Glockler and C. E. Morrell, J. Chem. Phys. **4**, 15 (1936).
[8] M. de Hemptinne, J. Jungers and J. M. Delfosse, J. Chem. Phys. **6**, 319 (1938). Cf. C. Manneback and A. Verleysen, Ann. Soc. Scient. Bruxelles **B56**, 349 (1936). Y. L. Tchang, Ann. Soc. Scient. Bruxelles Ser. I, **58**, 87 (1938).
[9] F. Stitt, J. Chem. Phys. **7**, 297 (1939).
[10] O. Redlich, Zeits. f. physik. Chemie **B28**, 371 (1935). O. Redlich and F. Pordes, Sitz. Ber. Akad. Wiss. Wien, IIb **145**, 67 (1936) or Monatsh. Chemie **67**, 203 (1936). Cf. R. W. Wood and D. H. Rank, Phys. Rev. **47**, 492 (1935) and A. Dadieu and W. Engler, Wiener Anzeiger, Math. Naturwiss. Abt. 176 (1935).
[11] O. Redlich and W. Stricks, Sitz. Ber. Akad. Wiss. Wien, IIb **145**, 192 (1936) or Monatsh. Chemie **67**, 328 (1936).
[12] B. Trumpy, Zeits. f. Physik **100**, 250 (1936).
[13] B. Trumpy, Zeits. f. Physik **98**, 672 (1936).
[14] S. Mizushima, Y. Morino and S. Sugiura, Proc. Imp. Acad. Tokyo **14**, 250 (1938). M. de Hemptinne and C. Velghe, Physica **5**, 958 (1938).
[15] E. S. Ebers and H. H. Nielsen, J. Chem. Phys. **6**, 311 (1938).
[16] A. Langseth and R. C. Lord, Jr., K. Danske Vidensk. Selskab. Math. fys. Medd. **16**, No. 6 (1938). C. K. Ingold *et al.* J. Chem. Soc. London 925, 966, 971 (1936), Nature (London) **139**, 880 (1937). R. W. Wood, J. Chem. Phys. **3**, 444 (1935). O. Redlich and W. Stricks, Sitz. Ber. Akad. Wiss. Wien, IIb **145**, 77 (1936) or Monatsh. Chemie **67**, 213 (1936).
[17] Referred to *p*-$C_6H_4D_2$ not to C_6H_6.

The Infra-Red Absorption of Hydrogen Fluoride

Imes[1] observed the infra-red absorption spectrum with the characteristic rotational structure of the P and R branches, for monomeric hydrogen fluoride. Because of the presence of water vapor he made no observations at longer wave-lengths. Since hydrogen fluoride is known to be highly associated in the vapor state because of hydrogen bonding, it seemed desirable to investigate the absorption spectrum thoroughly. We have done this with both the prism and grating spectrometer, for hydrogen fluoride in the vapor state and in carbon tetrachloride solution. The results of Imes were of course confirmed. At longer wave-lengths a very strong absorption is observed at higher pressures which we attribute to association. This absorption has several

maxima but the two main ones of equal intensity are at 2.95, and 2.87μ respectively.

The hydrogen fluoride spectrum in an inert solvent is of great interest since hydrogen fluoride has the lowest moment of inertia of any diatomic molecule which gives a rotation-vibration spectrum and some indication of rotational structure might be anticipated in solution. The spectrum as observed in carbon tetrachloride solution shows two very interesting features. In the first place there is no evidence of association, although the solubility is considerable. Water shows no association in carbon tetrachloride solution but water shows no association in the vapor state which is in equilibrium with the solution. Alcohols of course show strong association in carbon tetrachloride solution.

The absorption spectrum in solution as determined by a prism spectrometer appears to resemble, at first glance, the single molecule vapor spectrum, but a closer investigation shows that there are probably three absorption maxima instead of two and that one of these, the middle component is greatly magnified in intensity. A similar spectrum is found for hydrogen chloride. With the grating, evidence of fine structure is found. The complete results of this investigation will be published in the near future.

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[1] Imes, Astrophys. J. **50**, 251 (1919).

Sulfur Bands and an Attempt to Obtain HS Bands

Sometime ago we noticed that the band spectrum of the HS radical had not been observed. We have studied several sulfur compounds attempting to obtain such bands but the recent work of Lewis and White[1] indicates that it will be difficult to produce them in emission.

In every case investigated the sulfur band systems[2] appeared on our plates. The following gases and mixtures were passed through an 8000-volt uncondensed discharge at pressures ranging from 0.1 to 20 mm Hg.

(1) H_2S
(2) H_2S+H_2
(3) H_2+S (at various S concentrations)
(4) H_2+H_2S+S
(5) H_2S_2
(6) $H_2S_2+H_2$
(7) H_2S_2
(8) $H_2S_2+H_2$
(9) $S_2Cl_2+H_2$
(10) $S_2Cl_2+H_2+H_2S$
(11) $SOCl_2+H_2$
(12) $SOCl_2+H_2+H_2S$

The spectrum of the H_2S-O_2 flame was also studied.

Systems 1 to 4 are obvious attempts while the use of hydrogen disulfide[3] was suggested by the production of intense OH bands from hydrogen peroxide by Dawson and Johnston.[4] Again we observed the usual sulfur bands. The HS band found by Lewis and White[1] at 3237A in absorption falls in a relatively clear portion of the tail of the sulfur band at 3216A. Some of our plates appeared to show a very slight darkening at this point but this indication was not definite enough for analysis.

Our findings attest to the great instability of the HS radical.

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[1] M. N. Lewis and J. U. White, Phys. Rev. **55**, 894 (1939).
[2] See references in H. Spaner, *Molekulspektren* (Julius Springer, Berlin, 1935), Vol. I, p. 61.
[3] K. H. Butler and O. Maas, J. Am. Chem. Soc. **52**, 2184 (1930).
[4] D. H. Dawson and H. L. Johnston, Phys. Rev. **43**, 980 (1933).

Errata: On Transport Phenomena in the Cage Model of Liquids*

(J. Chem. Phys. **7**, 202 (1939))

Equation (2) should read

$$\eta=\frac{f\sigma}{\Delta v}=\frac{f\sigma}{a(m_+-m_-)}.$$

In the third line after Eq. (2) read $\pm fqa/2$ instead of $\pm lga/2$. In the eighth line after Eq. (2) read $\pm f$ rather than $\pm l$. The formula in the tenth line after Eq. (2) should read

$$m_+-m_-=\frac{m_0}{6}(e^{fqa/2kT}-e^{-fqa/2kT})=\frac{m_0}{6}\frac{fqa}{kT}.$$

Eq. (3) should read

$$\eta=kT\sigma/qD.$$

In the seventh line after Eq. (3) read $q\sigma=V/N$ rather than $g\sigma=V/N$.

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